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Using waste poly(vinyl chloride) to synthesize chloroarenes by plasticizer-mediated electro(de)chlorination

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Supporting Information for:

Using waste poly(vinyl chloride) to synthesize chloroarenes by plasticizer-mediated electro(de)chlorination.

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I. Materials

Poly(vinyl chloride) (PVC) was obtained from Sigma Aldrich and Tygon Tubing ®. Sigma Aldrich: PVC listed: M_w: ~233,000, M_n: ~99,000 (product #: 346764, lot # MKBW2191V), PVC listed: M_w: ~80,000, M_n: ~47,000 (product #: 389323, lot # MKCC7597), PVC listed: M_w: ~43,000, M_n: ~22,000 (product #: 389293, lot # MKCH4545). Tygon Tubing ®: PVC tubing (Formulation: B-44-3, product #: 389293, lot # MKCH4545, inner diameter: 1/8 inch, outer diameter: 1/4 inch, wall thickness: 1/16 inch.

The following reagents were used as received. From Sigma Aldrich: di(2-ethylhexyl) phthalate (lot # MKCK4506), ethoxybenzene, tridecane, 4'-chloroacetanilide, 1,3,5-triethylbenzene, caffeine, 2-chlorophenol, 4-chlorophenol, 4-phenylphenol, diisopropyl azodicarboxylate, triphenylphosphine, hydrochloric acid. From Oakwood Chemical: 1-phenylimidazole, 1-methyl-1H-indole, methyl phenoxyacetate, *N*,*N*-dimethylaminoethanol, (2,2,6,6-tetramethylpiperidin-1-yl)oxyl. From TCI: 3-methylbenzo[b]thiophene, 3-hexylthiophene, 2-phenyl[1,2-a]pyridine, 1-phenylpyrazole. From Fisher: triethylamine.

II. Experimental techniques

Nuclear Magnetic Resonance (NMR) Spectroscopy

Unless otherwise noted, ^{1}H and ^{13}C NMR spectra were acquired at rt. Chemical shift data are reported in units of δ (ppm) relative to tetramethylsilane (TMS). Spectra are referenced to residual solvent. Multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), triplet (t), quartet (q), multiplet (m).

High-Resolution Mass Spectrometry (HRMS)

High-resolution mass spectrometry data were obtained on a Micromass AutoSpec Ultima Magnetic Sector mass spectrometer.

Gas Chromatography–Mass Spectrometry (GC-MS)

GC-MS data was collected on Shimadzu GC-2010 gas chromatograph containing a Restek™ Rtx™-5 capillary columns with 15 m length, 0.25 mm inner diameter, 0.25 µm df (film thickness) with 5% diphenyl, 95% dimethsiloxane as the stationary phase, equipped with a Shimadzu GC-MS-QP2010S mass spectrometer. GC-MS data were analyzed using Shimadzu Corporation LabSolutions GC-MS solution Version 2.70 software. GC method: start and hold at 55 °C for 1 min, ramp 10 °C/min to 270 °C, hold at 270 °C for 10 min, total time = 32.5 min.

Sample work-up for GC-MS

A ~0.05 mL aliquot of crude reaction mixture was diluted with ~2 mL diethyl ether (Et_2O) and filtered through a silica gel plug and a PTFE filter (0.2 µm) into a GC vial.

Size-Exclusion Chromatography (SEC)

For SEC analysis, all polymers were dried under vacuum overnight, dissolved (~0.5 mg polymer/mL) in THF spiked with trace toluene as a flow marker (<1 vol%), and filtered through a PTFE filter (0.2 µm). Polymer molar masses were determined by comparison

with polystyrene standards (Varian, EasiCal PS-2 MW 580–377, 400) at 40 °C in THF on a Malvern Viscotek GPCMax VE2001 equipped with two Viscotek LT-5000L 8 mm (ID) × 300 mm (L) columns and analyzed with Viscotek TDA 305, or on a Shimadzu LC-20AD equipped with two Styragel HT 7.8 mm (ID) x 300 mm (L) columns and a PSS Gram column 8 mm (ID) x 300 mm (L) and analyzed with Shimadzu SPD-M20A. Data presented corresponds to the refractive index (RI) response normalized to the highest peak, and data were obtained at a flow rate of 1 mL/min.

Fourier-Transform Infrared (FTIR) Spectroscopy

FTIR spectroscopy data were obtained on neat samples using a Thermo-Nicolet IS-50 using the attenuated total reflectance (ATR) accessory.

Elemental Analysis (EA)

EA was performed by Atlantic Microlab, Inc.

Automatic Column Chromatography

Column chromatography was performed using a Biotage® Isolera™ One system and Biotage® Sfär Duo columns.

Thermogravimetric Analysis (TGA)

Thermogravimetric analysis (TGA) thermograms were recorded on a TA Instruments Q50 TGA. All experiments were conducted on platinum TGA sample pans under a nitrogen purge of 50 mL/min with a heating rate of 10 °C/min, covering a temperature range of 27 °C to 550 °C. The instrument was calibrated using the Curie points of alumel and nickel standards.

Differential Scanning Calorimetry (DSC)

DSC was performed under N_2 on a TA Instruments DSC Q2000 equipped with a TA RCS cooling accessory. Neat solid samples (~3–5 mg) were dried under vacuum overnight and then placed in aluminum Tzero Low-Mass Hermetic pans and sealed with Tzero Hermetic lids using a TA Instruments crimper. Samples were cycled between –50 °C and 200 °C at a ramp rate of 5 °C/min.

III. Characterization of PVC sources

Molar mass of PVC samples

The number-average (M_n) and weight-average (M_w) molar masses of each PVC source were measured by SEC. The measured values were different from the manufacturer listed values, and used to describe each PVC source herein, as highlighted in Table S1.

Table S1. List of PVC sources used in this work and the molar masses measured by SEC.

PVC	Source and Product Info	measured M_n (kg/mol)	measured M_w (kg/mol)	dispersity, $Đ_M$
PVC_{100k}	Sigma Aldrich listed: M_w: ~233,000; M_n: ~99,000	100	318	2.57
PVC_{47k}	Sigma Aldrich listed: M_w: ~80,000; M_n: ~47,000	47	100	2.08
PVC_{35k}	Sigma Aldrich listed: M_w: ~43,000; M_n: ~22,000	35	67	2.08
PVC_{tubing}, PVC_{solid}	Tygon Tubing	83	191	2.42

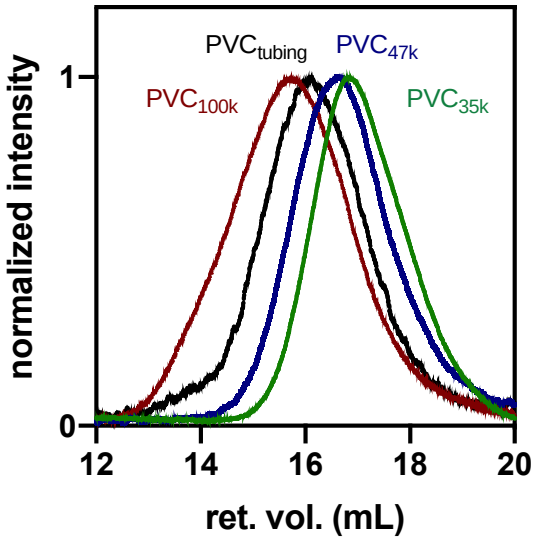


Figure S1. Normalized SEC traces of PVC samples.

Characterization of PVC_{tubing}

Extraction of plasticizer from Tygon tubing. A strip of Tygon tubing (4.145 g) was cut into small pieces (~0.5 cm length) and stirred in THF (~50 mL) at rt until fully dissolved (~30 min). The polymer was precipitated by pouring into cold methanol (~200 mL) while stirring. The polymer was collected by filtration, and the filtrate was concentrated under reduced pressure to give PVC_{solid}. This dissolution and precipitation process was repeated on the filtered polymer 2 more times. The combined filtrates were concentrated under reduced pressured and further dried under vacuum overnight to remove residual solvent. A colorless oil was obtained (1.308 g, 32% mass rel. to tubing input, 1:14 mol ratio DEHP:PVC repeat unit). NMR signals and GC retention times of extract matched commercial DEHP standard. Note, the commercial DEHP standard purchased from Sigma Aldrich is labeled “di(octyl) phthalate” by the supplier, but it is di(2-ethylhexyl) phthalate (see NMR evidence below).

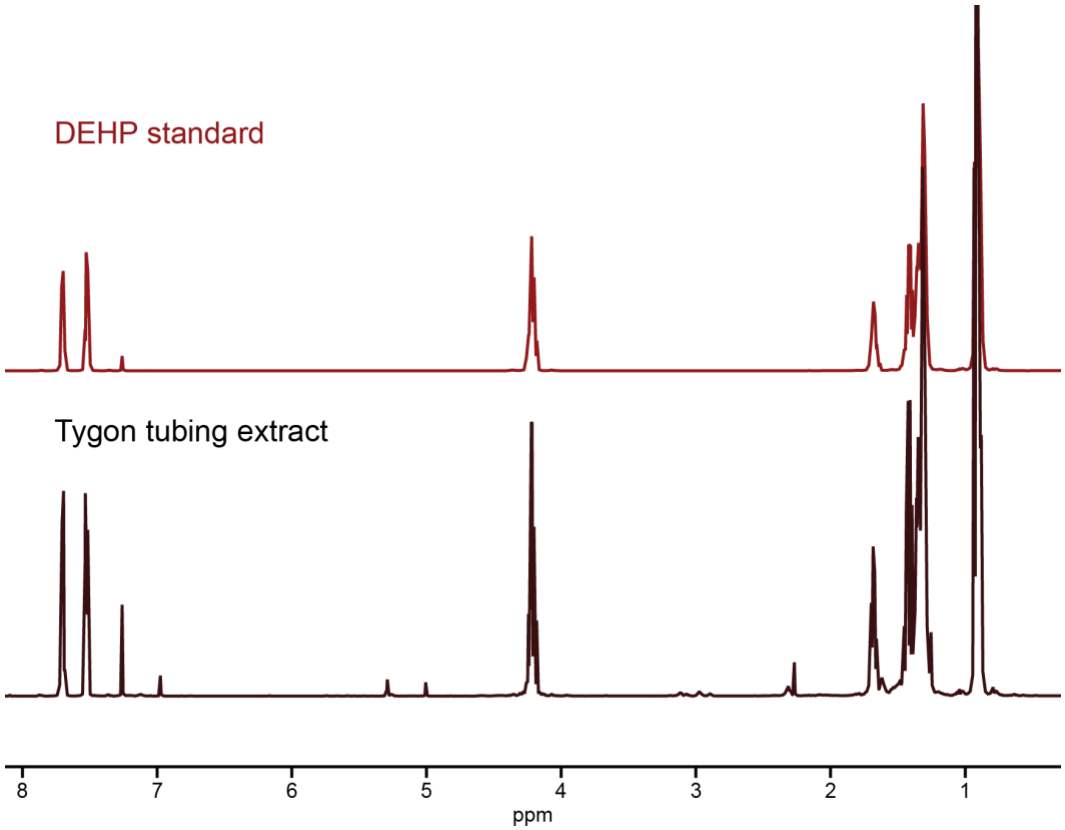


Figure S2. Stacked ^{1}H NMR spectra of DEHP standard (Sigma Aldrich) and liquid extracted from Tygon tubing sample. DEHP standard ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.55 – 7.49 (m, 2H), 4.28 – 4.16 (m, 4H), 1.74 – 1.61 (m, 2H), 1.49 – 1.24 (m, 16H), 0.97 – 0.84 (m, 12H). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.56 – 7.49 (m, 2H), 4.27 – 4.16 (m, 4H), 1.76 – 1.63 (m, 2H), 1.51 – 1.24 (m, 16H), 0.96 – 0.85 (m, 12H).

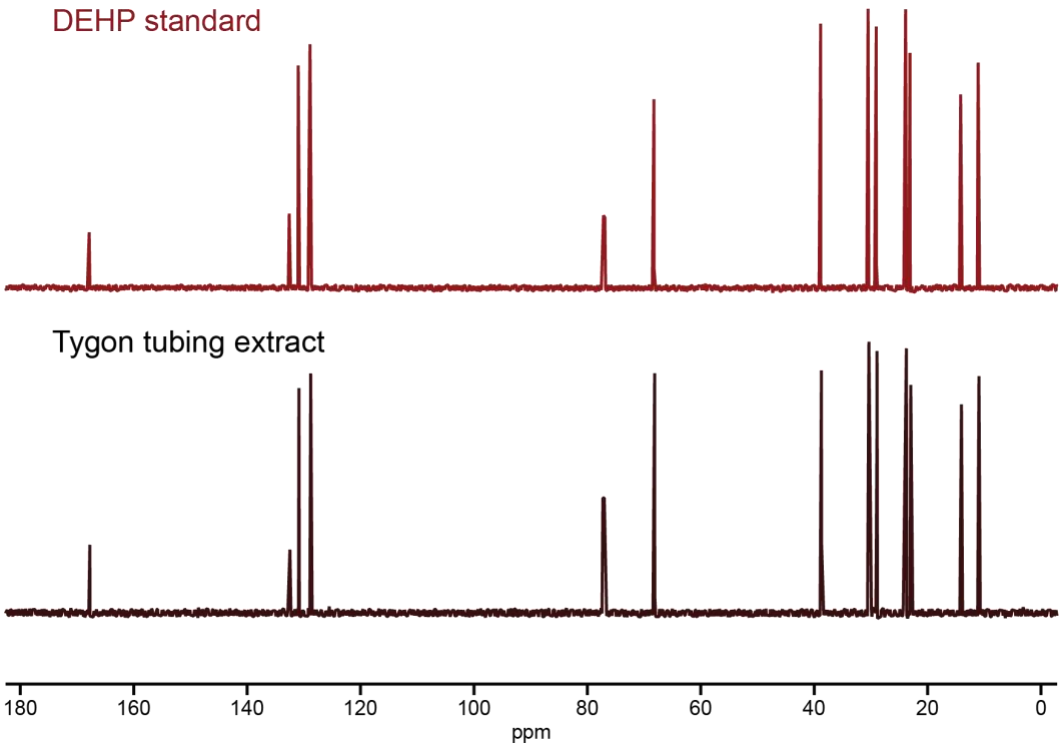


Figure S3. Stacked ^{13}C NMR spectra of DEHP standard (Sigma Aldrich) and liquid extracted from Tygon tubing sample. DEHP standard ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.85, 132.58, 130.98, 128.91, 68.26, 38.86, 30.49, 29.05, 23.88, 23.11, 14.17, 11.08. Tygon tubing extract ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.88, 132.60, 131.01, 128.93, 68.28, 38.87, 30.50, 29.06, 23.88, 23.12, 14.18, 11.09.

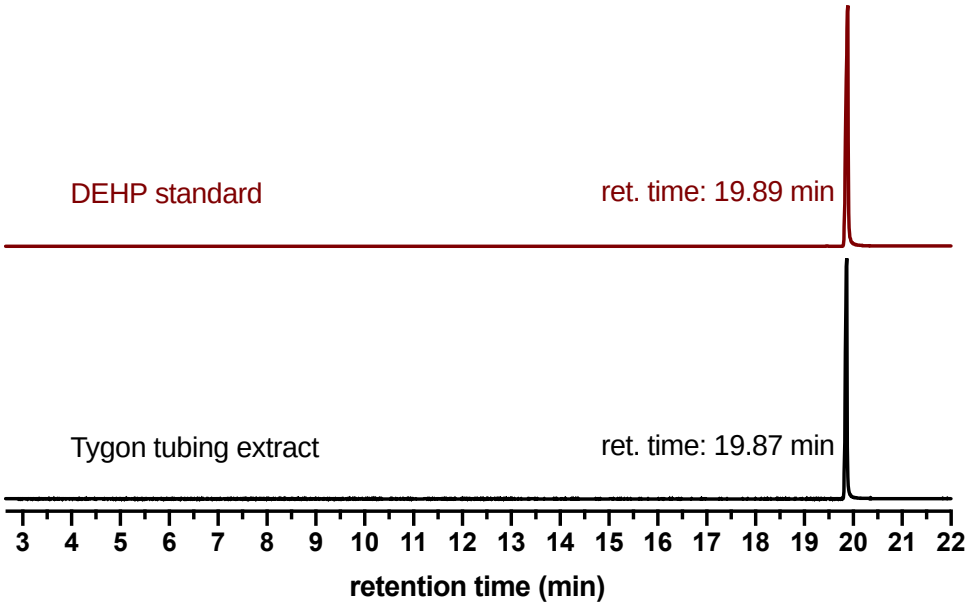


Figure S4. Stacked GC-MS chromatograms of DEHP standard (Sigma Aldrich) and liquid extracted from Tygon tubing sample.

IV. Optimization of paired dehydrochlorination–chlorination reaction

General Procedure A (undivided cell paired electrolysis, constant current, 3 mL scale)

PVC (65 mg, 1.0 mmol (repeat unit), 8.0 equiv. (repeat unit)), NBu_4BF_4 (314 mg, 0.95 mmol), DEHP (0.050 mL, 0.13 mmol, 1.0 equiv.), ethoxybenzene (0.015 mL, 0.13 mmol, 1.0 equiv.), tridecane internal standard (0.010 mL), and DMF (3 mL) were added to a 5 mL *ElectraSyn*® reaction vessel equipped with Teflon coated magnetic stir bar (cylindrical, 12.7 mm length) and two graphite electrodes (0.8 x 0.2 x 5.20 cm). All reagents were dissolved by stirring for at least 15 min, then the reaction mixture was subjected to constant current electrolysis (3 or 7 mA, as specified in Table S2. Survey of current strength on a 3 mL scale paired-electrolysis reaction.) with alternating polarity (15 min) at rt. The reaction was stirred at 400 rpm for 5–10 h.

General Procedure B (undivided cell paired electrolysis, constant voltage, 3 mL scale)

PVC (65 mg, 1.0 mmol (repeat unit), 8.0 equiv. (repeat unit)), NBu_4BF_4 (314 mg, 0.95 mmol), DEHP (0.050 mL, 0.13 mmol, 1.0 equiv.), ethoxybenzene (0.015 mL, 0.13 mmol, 1 equiv.), tridecane internal standard (0.010 mL), and DMF (3 mL) were added to a 5 mL *ElectraSyn*® reaction vessel equipped with Teflon coated magnetic stir bar (cylindrical, 12.7 mm length), two graphite electrodes (0.8 x 0.2 x 5.20 cm), and a silver wire reference electrode stored in 3 M KCl in water. All reagents were dissolved by stirring for at least 15 min, then the reaction mixture was subjected to constant voltage electrolysis (−1.1, −1.2, −1.3, or −2.0 V, as specified in Table S3) with alternating polarity (15 min) at rt. The reaction was stirred at 400 rpm for 8 h.

General Procedure C (undivided cell paired electrolysis, constant current, 8 mL scale)

PVC (200 mg, 3.2 mmol (repeat unit), 8.1 equiv. (repeat unit)), NBu_4BF_4 (264 mg, 0.80 mmol), DEHP (0.157 mL, 0.4 mmol, 1.0 equiv.), ethoxybenzene (0.051 mL, 0.4 mmol), tridecane internal standard (0.050 mL), and DMF (8 mL) were added to a 10 mL *ElectraSyn*® reaction vessel equipped with Teflon coated magnetic stir bar (egg-shaped, 16 mm length) and two graphite electrodes (0.8 x 0.2 x 5.20 cm). All reagents were dissolved by stirring for at least 15 min, then the reaction mixture was subjected to constant current electrolysis (10 mA) with alternating polarity (15 min) at rt. The reaction was stirred at 400 rpm for 16 h.

General Procedure D (undivided cell paired electrolysis, constant voltage, 8 mL scale)

PVC (200 mg, 3.2 mmol (repeat unit), 8.1 equiv. (repeat unit)), NBu_4BF_4 (264 g, 0.80 mmol), DEHP (0.157 mL, 0.4 mmol, 1.0 equiv.), ethoxybenzene (0.4 mmol), tridecane internal standard (0.050 mL), and DMF (8 mL) were added to a 10 mL *ElectraSyn*® reaction vessel equipped with Teflon coated magnetic stir bar (egg-shaped, 16 mm length), two graphite electrodes (0.8 x 0.2 x 5.20 cm), and a silver wire reference electrode stored in 3 M KCl in water. All reagents were dissolved (or swelled) by stirring for at least

15 min, then the reaction mixture was subjected to constant voltage electrolysis (−1.3 V) with alternating polarity (15 min) at rt. The reaction was stirred at 400 rpm for 16 h.

Survey of current strength (smaller scale)

The reactions were set up according to General Procedure A and monitored by GC-MS. Details on the GC-MS analysis are described at the end of this section. As shown in Figure S5, once DEHP is consumed, the paired oxidative chlorination reaction tapers off. This information suggests that the rates of each half reaction (reduction and oxidation) should be matched. Note, the effect of operating currents varies with reaction scale. For example, the influence of 7 mA on a 3 mL reaction is different than 7 mA would be a on a larger scale. In forthcoming reactions on a larger scale (8 mL), 10 mA current was used.

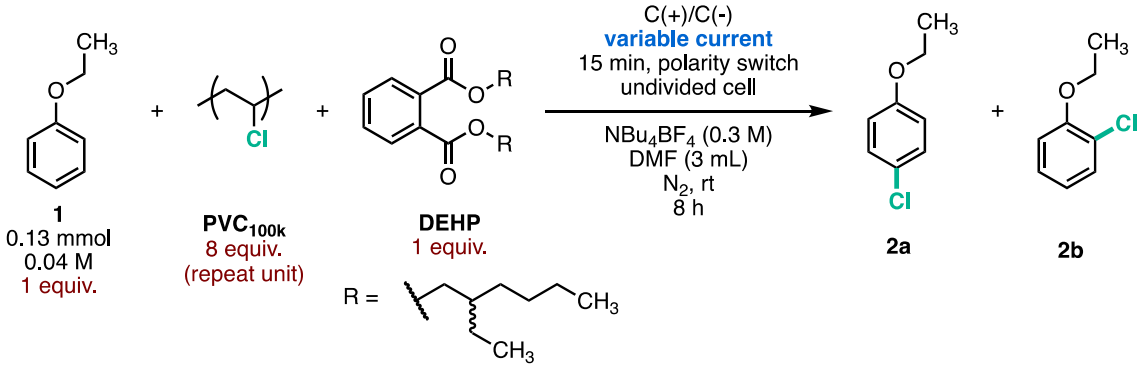


Table S2. Survey of current strength on a 3 mL scale paired-electrolysis reaction.

entry	conditions	conversion of **1** (%)	consumption of DEHP (%)	yield of **2** (%)
1	3 mA, 10 h	67	89	53
2	7 mA, 5 h	56	95	35

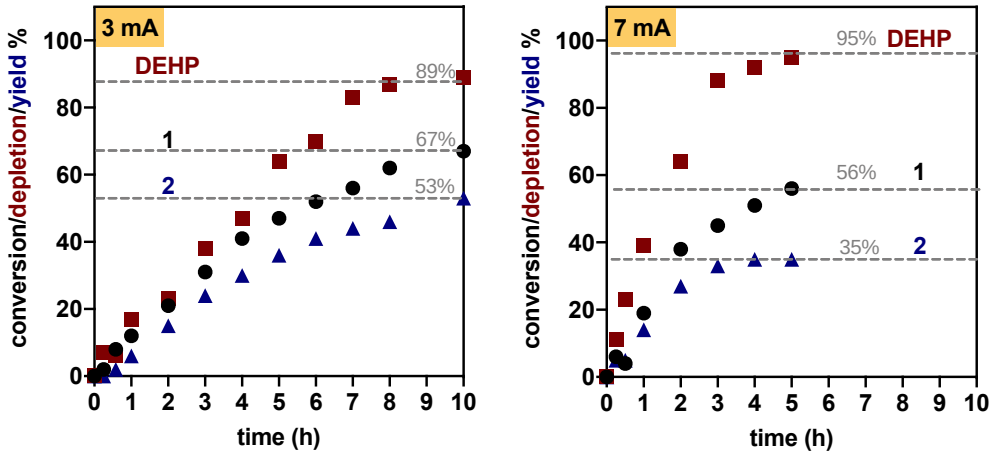


Figure S5. Monitoring conversion of **1** (●), consumption of **DEHP** (■), and yield of **2** (▲) over time under 3 mA (left) and 7 mA (right) constant current. Reactions were performed on a 3 mL scale under N_2.

Survey of voltages (smaller scale)

The reactions were set up according to General Procedure B and monitored by GC-MS. −1.3 V is the smallest voltage at which the reaction proceeds and is used in forthcoming constant voltage experiments. Note, this voltage is achieved using the potentiostat built into the IKA ElectraSyn, which differs from the potentiostat used in the cyclic voltammetry and bulk electrolysis studies.

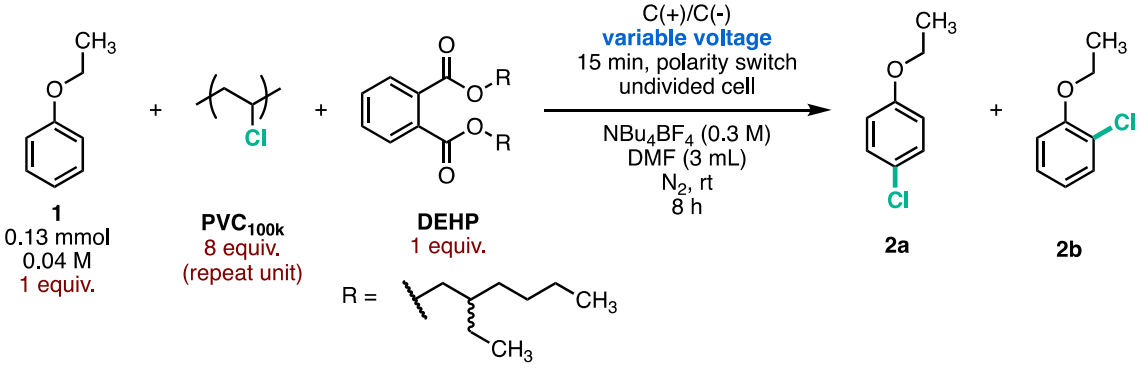


Table S3. Survey of voltage strength on a 3 mL scale paired-electrolysis reaction.

entry	conditions	conversion of **1** (%)	consumption of DEHP (%)	yield of **2** (%)
1	−1.1 V[a]	n.r.	n.r.	n.r.
2	−1.2 V[a]	n.r.	n.r.	n.r.
3	−1.3 V, 8 h	76	89	55
4	−2.0 V[b], 2 h	43	44	0

[a] Reaction auto shutdown in less than 15 min because the resistance was too high.
[b] Reaction was turned off after 2 h because no product was observed although starting material was being consumed.
n.r. = no reaction occurred

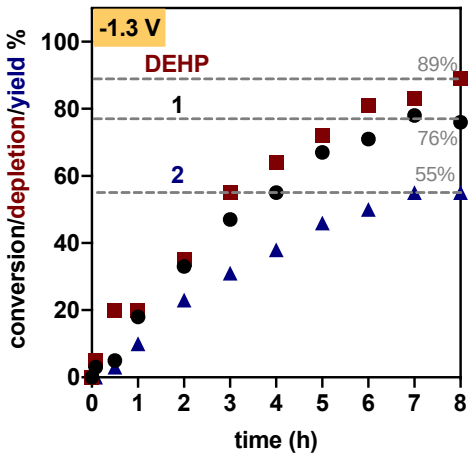


Figure S6. Monitoring conversion of **1**(●), consumption of **DEHP** (■), and yield of **2** (▲) over time under -1.3 V constant voltage. Reaction was performed on a 3 mL scale under N_2.

Survey of air versus N_2

The reactions were set up according to General Procedure C and monitored by GC-MS. Each set of conditions were run in duplicate. This data shows that this reaction proceeds to higher yields under air.

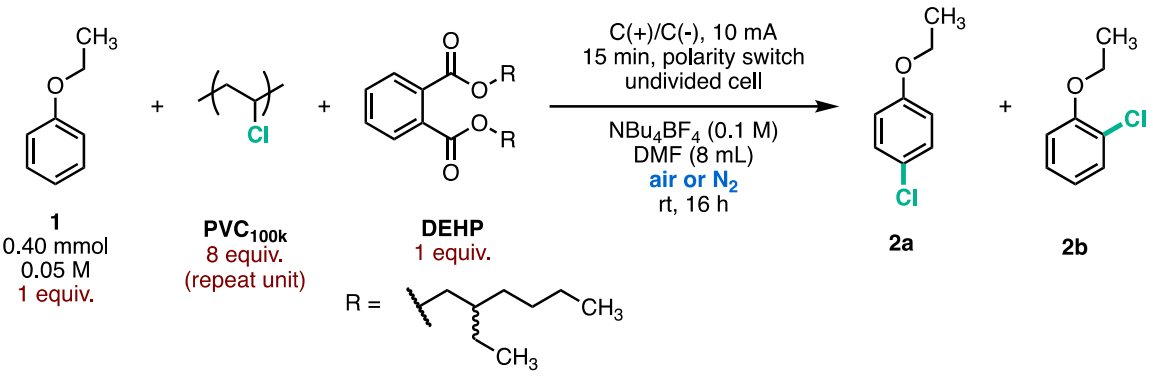


Table S4. Survey of air versus N_2 atmosphere on the paired-electrolysis reaction.

entry	conditions	conversion of **1** (%)	consumption of **DEHP** (%)	yield of **2** (%)
1	wet[a] DMF air	85, 93	99, 100	68, 77
2	anhydrous[b] DMF N_2	73, 79	97, 98	53, 54

[a] "Wet" DMF was stored in an opened bottle
[b] "Anhydrous" DMF was stored in sure/seal bottle

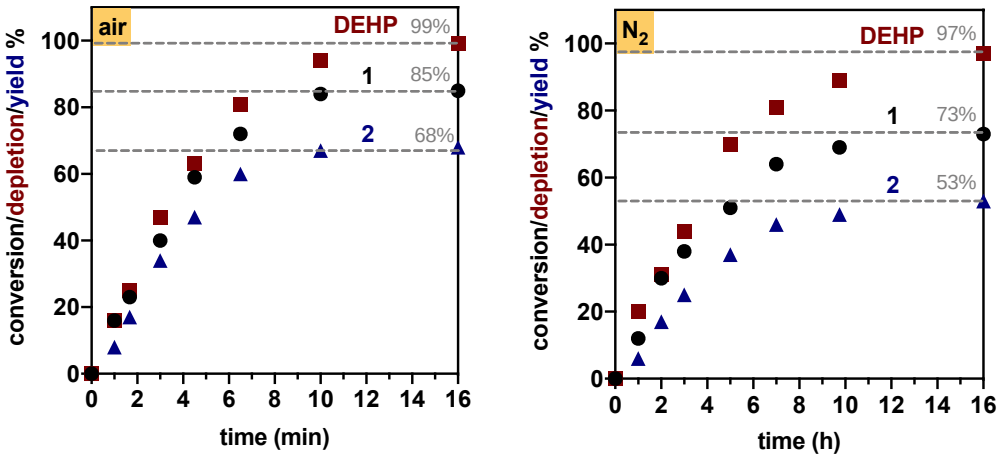


Figure S7. Monitoring conversion of (●), consumption of **DEHP** (■), and yield of **2** (▲) over time under air (left) and a N_2 atmosphere (right). Reactions were performed on an 8 mL scale.

Survey of PVC molecular weight and DEHP equivalents under galvanostatic conditions

The reactions were set up according to General Procedure C and monitored by GC-MS. Each set of conditions were run in duplicate. Tributylamine was only observed in the GC-MS traces of reactions performed without DEHP.

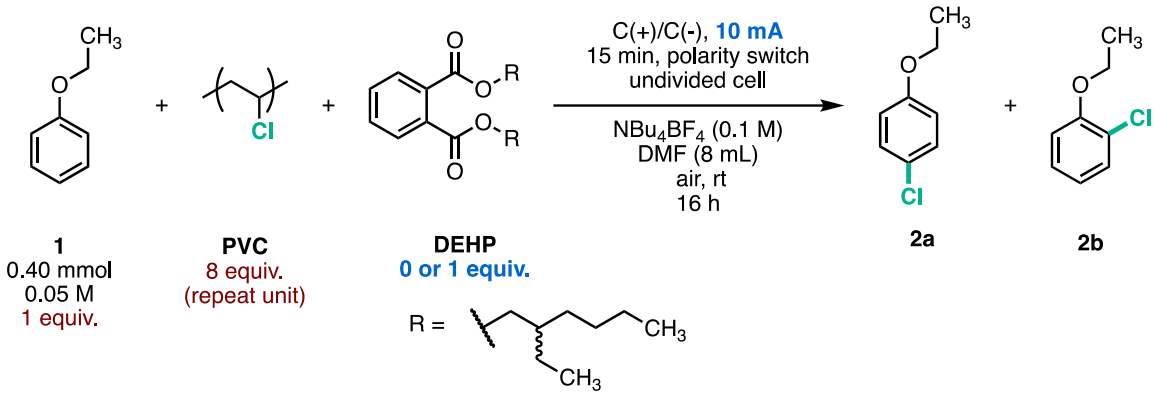


Table S5. Survey of effect of PVC molecular weight and presence of DEHP under constant current.

entry	**PVC** source	**PVC** equiv.	**DEHP** equiv.	conversion of **1** (%)	consumption of **DEHP** (%)	yield of **2** (%)	NBu_3
1	PVC_{100k}	8	0	53, 51	n/a	26, 31	y, y
2	PVC_{100k}	8	1	85, 93	99, 100	68, 77	n, n
3	PVC_{47k}	8	0	76, 71	n/a	52, 59	y, y
4	PVC_{47k}	8	1	97, 99	96, 99	78, 92	n, n
5	PVC_{35k}	8	0	95, 100	n/a	86, 89	y, y
6	PVC_{35k}	8	1	99, 99	94, 97	74, 75	n, n

n/a = not applicable because reagent was not used in this reaction

Survey of PVC molecular weight and DEHP equivalents under potentiostatic conditions

The reactions were set up according to General Procedure D and monitored by GC-MS. Each set of conditions were run in duplicate. Reactions auto shutdown when there was no DEHP present in the reaction mixture because the resistance was too high. Tributyl amine was observed in the GC-MS traces of all reactions where conversion is observed.

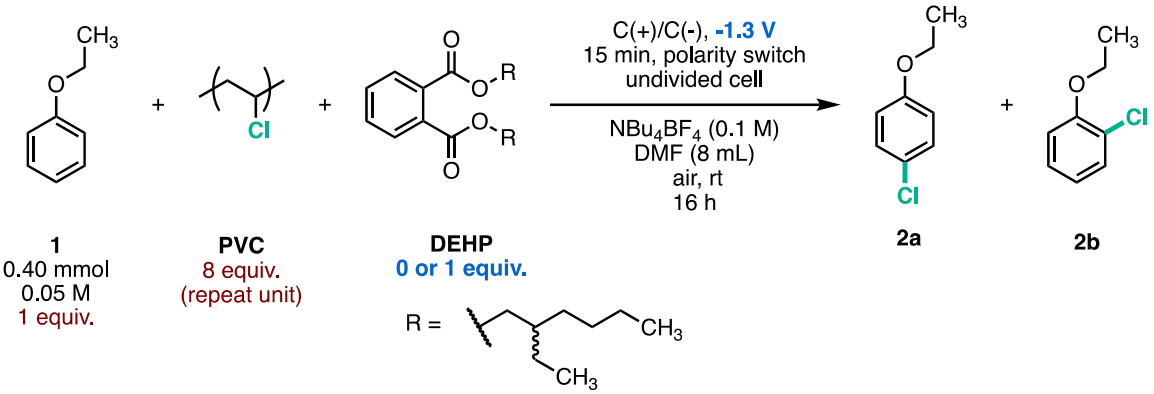


Table S6. Survey of effect of PVC molecular weight and presence of DEHP under constant voltage.

entry	**PVC** source	**PVC** equiv.	**DEHP** equiv.	conversion of **1** (%)	consumption of **DEHP** (%)	yield of **2** (%)	NBu_3
1	PVC_{100k}	8	0	n.r.	n/a	n.r.	n.r.
2	PVC_{100k}	8	1	84, 73	83, 77	54, 41	y, y
3	PVC_{47k}	8	0	n.r.	n/a	n.r.	n.r.
4	PVC_{47k}	8	1	88, 81	98, 94	57, 46	y, y
5	PVC_{35k}	8	0	n.r.	n/a	n.r.	n.r.
6	PVC_{35k}	8	1	73, 82	94, 99	36, 48	y, y

n.r. = no reaction occurred
n/a = not applicable because reagent was not used in this reaction

GC-MS Analysis

GC-MS data was collected for several chemical standards and used as references for retention times. The mass spectrum of each sample matched >90% with spectra in Shimadzu mass-spec library.

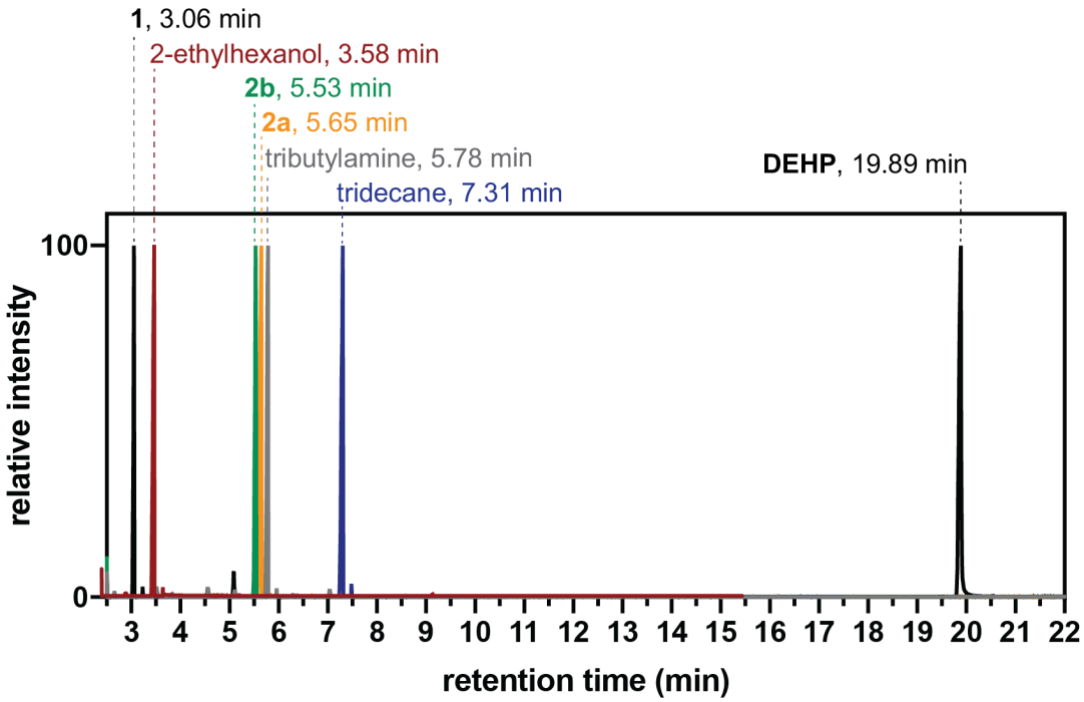


Figure S8. Overlaid GC-MS chromatograms of chemical standards relevant to this work.

GC-MS response factors of products 4-chloro-1-ethoxybenzene (**2a**) and 4-chloro-1-ethoxybenzene (**2b**) vs. starting material ethoxybenzene (**1**) were calculated using the molar response measured from the GC peak areas of known solution concentrations (eq. 1).

$$response\ factor = \frac{molar\ response\ of\ 2a\ or\ 2b}{molar\ response\ of 1} = \frac{area/concentration}{area/concentration} \qquad (eq.\ 1)$$

Six solutions of known concentrations were prepared according to volumes listed in the table below. For each, the indicated amount of analyte **1**, **2a**, or **2b** was dispensed from a micropipette into a 25 mL volumetric flask and then diluted with acetone. Two GC-MS traces were taken for each solution, generating 12 total molar response data points for each analyte. These data points were used calculate average response factors for **2a** vs. **1** and **2b** vs. **1**.

response factor of **2a** vs. **1** = **1.17 ± 0.07**

response factor of **2b** vs. **1** = **1.16 ± 0.05**

Table S7. Data used to calculate GC-MS response factors, including sample preparation measurements and data extracted from chromatograms.

solution	analyte	vol. added (μL)	concentration (M)[a]	trial	GC peak area	molar response	response factor vs. 1
1	1	10	0.00315	1	6753561	2146416616	1.00
				2	7862605	2498892957	1.00
	2a	10	0.00286	1	6660478	2327511290	1.08
				2	7598539	2655317728	1.06
	2b	10	0.00288	1	6923597	2401454036	1.12
				2	7875972	2731785912	1.09
2	1	12	0.00378	1	8167544	2163173887	1.00
				2	7462957	1976564032	1.00
	2a	12	0.00343	1	9236690	2689809482	1.24
				2	8002472	2330393795	1.18
	2b	12	0.00346	1	8717753	2519798491	1.17
				2	7684397	2221115001	1.12
3	1	14	0.00441	1	6785241	1540346538	1.00
				2	7603729	1726154995	1.00
	2a	14	0.00401	1	7755426	1935815758	1.26
				2	8100810	2022026340	1.17
	2b	14	0.00404	1	7443360	1844095831	1.20
				2	8026028	1988452094	1.15
4	1	16	0.00503	1	10251061	2036244996	1.00
				2	11508964	2286111687	1.00
	2a	16	0.00458	1	10215492	2231134252	1.10
				2	11783768	2573656599	1.13
	2b	16	0.00461	1	10468225	2269319074	1.11
				2	12033682	2608681423	1.14
5	1	18	0.00566	1	11447268	2021205821	1.00
				2	10998116	1941900555	1.00
	2a	18	0.00515	1	13374301	2596480026	1.29
				2	12206113	2369688599	1.22
	2b	18	0.00519	1	13184267	2540539677	1.26
				2	11978904	2308272496	1.19
6	1	20	0.00629	1	10923164	1735799878	1.00
				2	9146106	1453407609	1.00
	2a	20	0.00572	1	11357821	1984501458	1.14
				2	10118519	1767963741	1.22
	2b	20	0.00577	1	11581444	2008515619	1.16
				2	10135133	1757688673	1.21

[a] Concentrations were calculated for a total volume of 25 mL. The densities of **1**, **2a**, and **2b** (0.961, 1.1204, and 1.1288 g/mL, respectively) were taken from the literature and used to calculate concentration.[1] The molecular weights of **1**, **2a**, and **2b** (122.17, 156.61, and 156.61 g/mol, respectively) were also used to calculate concentration.

For each reaction, GC-MS was taken before electrolysis (0 min) and after electrolysis (typically 16 h). Representative chromatograms and peak integration area data is shown below. Tridecane was used as an internal standard.

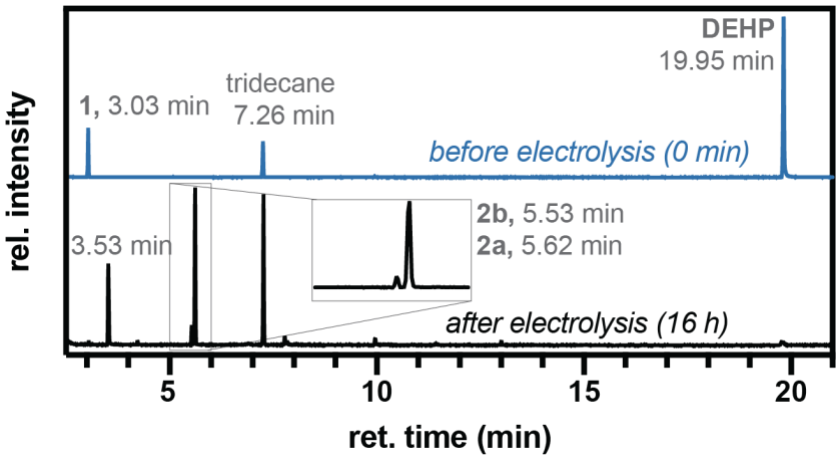


Figure S9. Representative GC-MS collected before and after the electrochemical reaction performed according to General Procedure C, using PVC_{47k} and 1 equiv. of DEHP under 10 mA constant current. GC-MS peak at 3.53 min matches with 2-ethylhexanol.

Table S8. Raw data extracted from representative GC-MS chromatograms from 10 mA constant current electrolysis with PVC_{47k} and 1 equiv. of DEHP.

	GC-MS peak area	
compound	**0 min**	**16 h**
1	2295449	25293
2b	0	264078
2a	0	2126567
tributyl amine	0	0
tridecane	2061868	2007309
DEHP	12497710	107637

The fraction of each analyte (**1**, **2a**, **2b**, and **DEHP**) relative to the internal standard (tridecane) was calculated for each using the following equation:

$$fraction\ relative\ to\ standard = \frac{area_{analyte}}{area_{internal\ standard}} \qquad (eq.\ 2)$$

Table S9. Representative GC-MS data normalized to tridecane internal standard.

	fraction relative to standard	
compound	**0 min**	**16 h**
1	1.113	0.013
DEHP	6.061	0.054
2b	0.000	0.132
2a	0.000	1.059

The percent of **1** converted during electrolysis was determined using the following equation:

$$\%\ of\ 1\ converted = \left(1 - \frac{fraction\ of\ 1\ at\ 16\ h}{fraction\ of\ 1\ at\ 0\ min}\right) \times 100\% \qquad \textit{(eq. 3)}$$

The percent of **DEHP** consumed during electrolysis was determined using the following equation:

$$\%\ of\ DEHP\ consumed = \left(1 - \frac{fraction\ of\ DEHP\ at\ 16h}{fraction\ of\ DEHP\ at\ 0\ min}\right) \times 100\% \qquad \textit{(eq. 4)}$$

The relative percent of **2a** generated during electrolysis (% yield) was determined using the following equation, in which 1.17 is used as the response factor for **2a** vs. **1**:

$$\%\ yield\ of\ 2a = \left(\frac{fraction\ of\ 2a\ at\ 16\ h}{1.17 * fraction\ of\ 1\ at\ 0\ min}\right) \times 100\% \qquad \textit{(eq. 5)}$$

The relative percent of **2b** generated during electrolysis (% yield) was determined using the following equation, in which 1.16 is included as the response factor for **2b** vs. **1**:

$$\%\ yield\ of\ 2b = \left(\frac{fraction\ of\ 2b\ at\ 16h}{1.16 * fraction\ of\ 1\ at\ 0\ min}\right) \times 100\% \qquad \textit{(eq. 6)}$$

The total yield of **2** was determined by adding the individual yields of **2a** and **2b**.

$$total\ \%\ yield\ of\ 2 = \%\ yield\ of\ 2a + \%\ yield\ of\ 2b \qquad \textit{(eq. 7)}$$

Table S10. Final values determined from representative GC-MS data from 10 mA constant current electrolysis with PVC_{47k} and 1 equiv. of DEHP.

	% converted, consumed, or generated	
compound	**0 min**	**16 h**
1	0	99
DEHP	0	99
2b	0	10
2a	0	81
total yield of 2	**-**	**92**

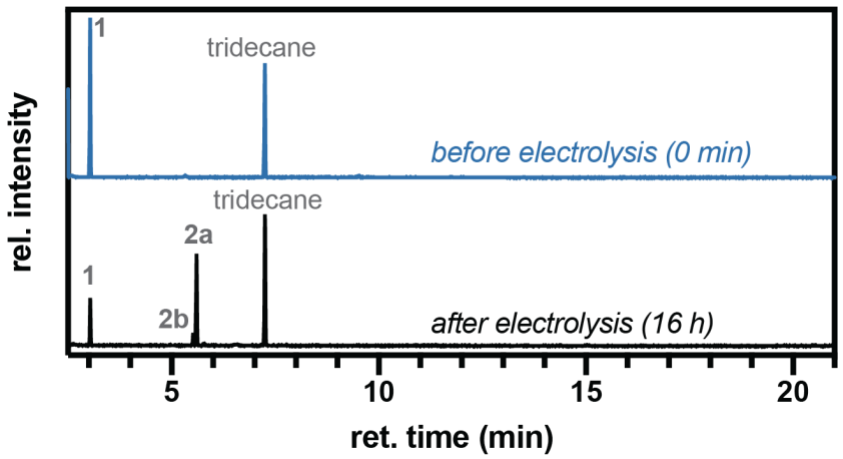


Figure S10. Representative GC-MS collected before and after the electrochemical reaction performed according to General Procedure C, using PVC_{47k} and 0 equiv. of DEHP under 10 mA constant current. Note, no material eluted after 21 min.

Table S11. Raw data extracted from representative GC-MS chromatograms from 10 mA constant current electrolysis with PVC_{47k} and no DEHP.

	GC-MS peak area	
compound	**0 min**	**16 h**
1	3332164	541219
2b	0	168956
2a	0	1178574
tributyl amine	0	40544
tridecane	2818302	1872548
DEHP	0	0

Table S12. Final values determined from representative GC-MS data from 10 mA constant current electrolysis with PVC_{47k} and no DEHP.

	% converted, consumed, or generated	
compound	**0 min**	**16 h**
1	0	76
DEHP	-	-
2b	0	7
2a	0	45
total yield of 2	**-**	**52**

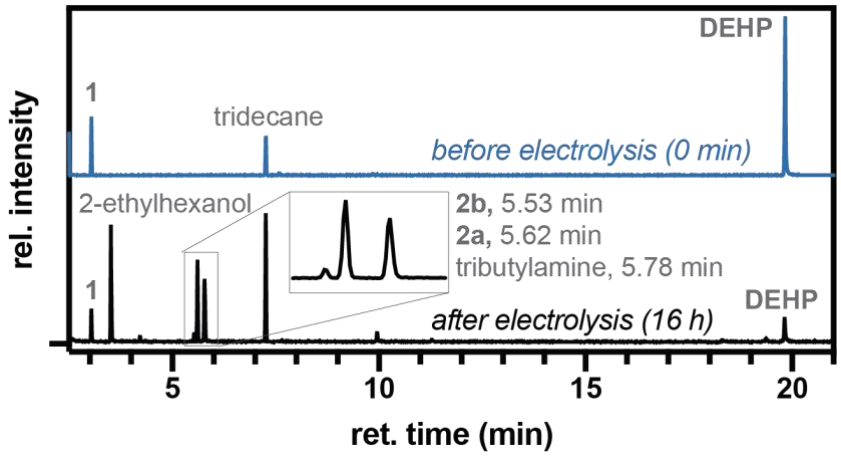


Figure S11. Representative GC-MS collected before and after the electrochemical reaction performed according to general procedure D, using PVC_{47k} and 1 equiv. of DEHP under −1.3 V constant voltage. Note, no material eluted after 21 min.

Table S13. Raw data extracted from representative GC-MS chromatograms from −1.3 V constant voltage electrolysis with PVC_{47k} and 1 equiv. DEHP.

	GC-MS peak area	
compound	**0 min**	**16 h**
1	2675738	418466
2b	0	123465
2a	0	1064898
tributyl amine	0	926672
tridecane	2178672	1793189
DEHP	10665027	521906

Table S14. Final values determined from representative GC-MS data from −1.3 V constant voltage electrolysis with PVC_{47k} and 1 equiv. DEHP.

	% converted, consumed, or generated	
compound	**0 min**	**16 h**
1	0	81
DEHP	0	94
2b	0	5
2a	0	41
total yield of 2	**-**	**46**

V. Cyclic voltammetry

Analysis of individual components

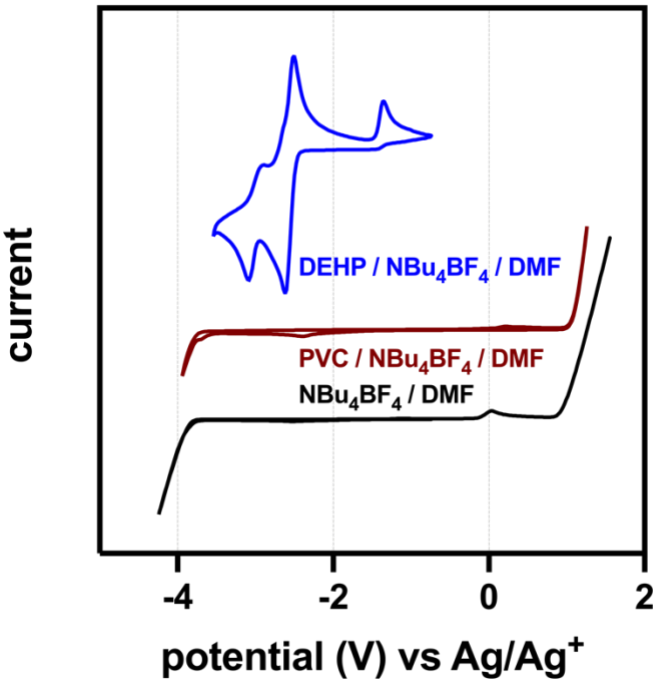


Figure S12. CVs of a blank solution (black —), 10 mM PVC_{35k} calculated per repeat unit (red —), and 10 mM DEHP (blue —). CVs were collected in 0.1 M NBu_4BF_4 in DMF using a 100 mV/s scan rate.

Analysis of mixed components

CVs of the first $1e^-$ redox couple of DEHP were collected in the presence of increasing equivalents of PVC. Equivalents were calculated by repeat unit mass and are effectively the same the number of C–Cl bonds. CVs were initially collected using a 10 mM concentration of DEHP (Figure S13, left). The concentration was reduced by 10-fold (1 mM DEHP; Figure S13, right) to minimize viscosity/diffusivity effects upon addition of excess polymer. Although attenuated at lower net concentrations, PVC still affected the reversibility of the $1e^-$ redox couple observed for DEHP. Control studies using polystyrene (average M_w: 35,000 g/mol, lot # MKCD6541) showed a negligible effect on the $1e^-$ redox couple observed for DEHP, suggesting changes in solution viscosity were not significant.

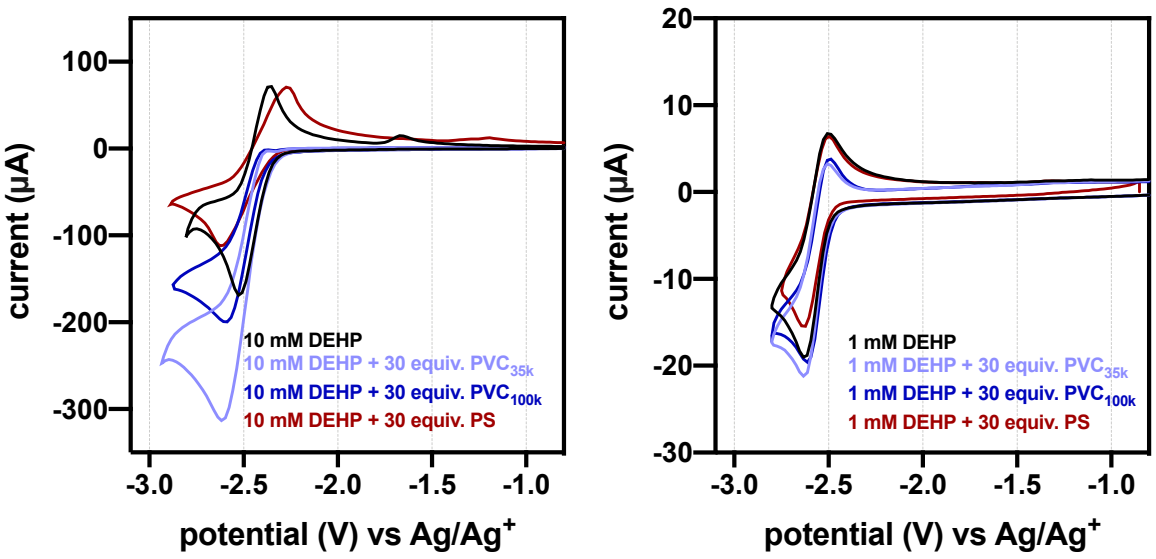


Figure S13. CVs of DEHP at 10 mM (left) and 1 mM (right) and DEHP mixed with 30 equiv. PVC_{35k}, PVC_{100k}, or PS. CVs were collected in 0.1 M NBu_4BF_4 in DMF using 100 mV/s scan rate.

Table S15. Raw data extracted from CV measurements of DEHP mixed with 30 equiv. PVC_{35k}, PVC_{100k}, or PS.

polymer added	10 mM DEHP			1 mM DEHP		
	i_{pa} (µA) oxidation	i_{pc} (µA) reduction	i_{pa} / i_{pc}	i_{pa} (µA) oxidation	i_{pc} (µA) reduction	i_{pa} / i_{pc}
none	92.0	168.8	0.54	10.3	17.3	0.59
PVC_{35k} (30 equiv.)	-	314.3	-	7.8	19.5	0.40
PVC_{100k} (30 equiv.)	-	199.1	-	7.9	18.0	0.44
PS (30 equiv.)	71.4	112.5	0.63	9.2	13.8	0.67

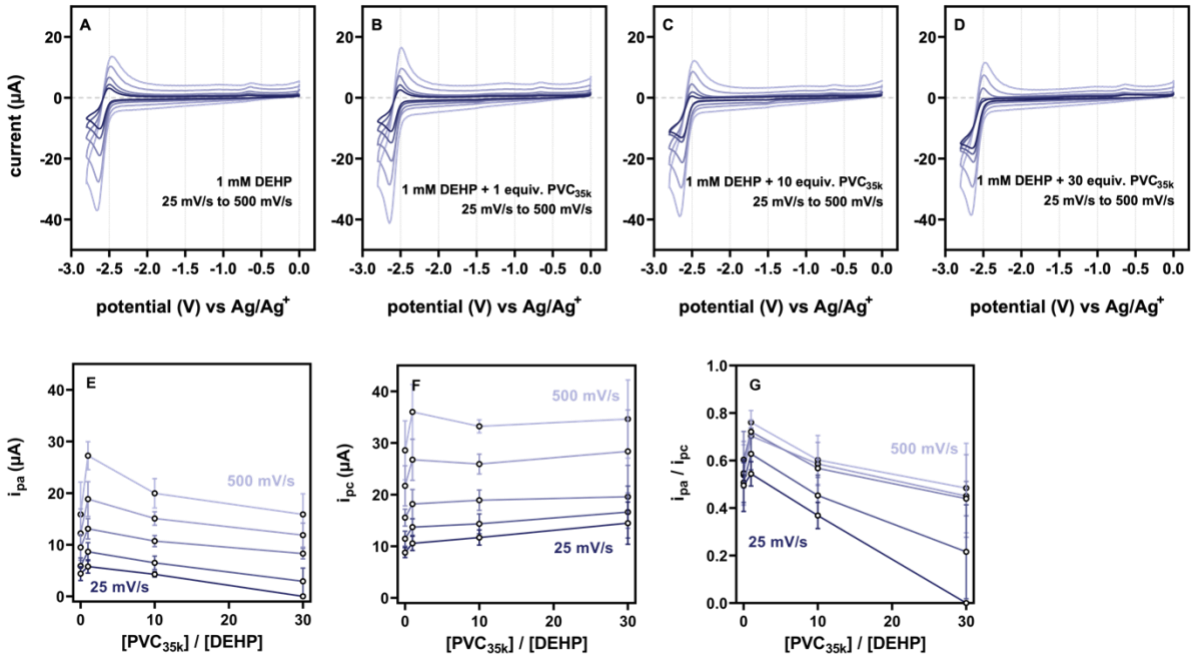


Figure S14. (A–D) Cyclic voltammetry of 1 mM DEHP in the presence of (A) 0 equiv. (B) 1 equiv. (C) 10 equiv. (D) 30 equiv. of PVC_{35k} with scan rates of 25, 50, 100, 250, 500 mV/s (darkest blue = 25 and lightest blue = 500 mV/s) (E) oxidation current (F) reduction current (G) oxidation/reduction. The averages and standard deviations (represented by the error bars) can be found in Table S16.

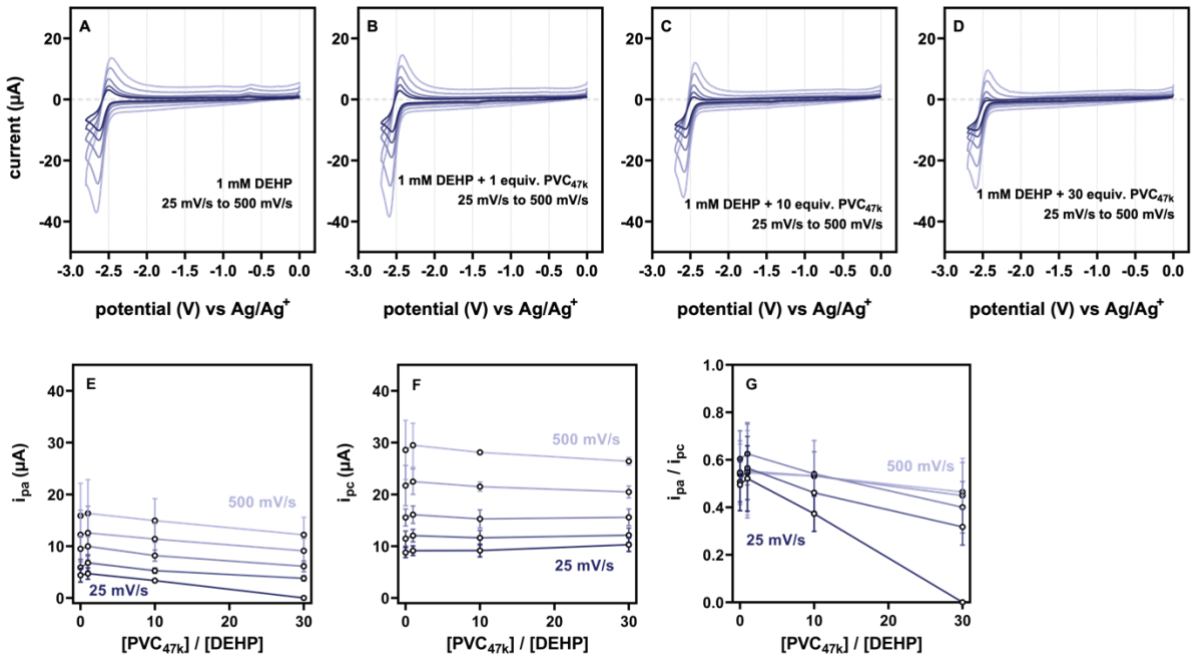


Figure S15. (A–D) Cyclic voltammetry of 1 mM DEHP in the presence of (A) 0 equiv. (B) 1 equiv. (C) 10 equiv. (D) 30 equiv. of PVC_{47k} with scan rates of 25, 50, 100, 250, 500 mV/s (darkest blue = 25 and lightest blue = 500 mV/s) (E) oxidation current (F) reduction

current (G) oxidation/reduction. The averages and standard deviations (represented by the error bars) can be found in Table S16.

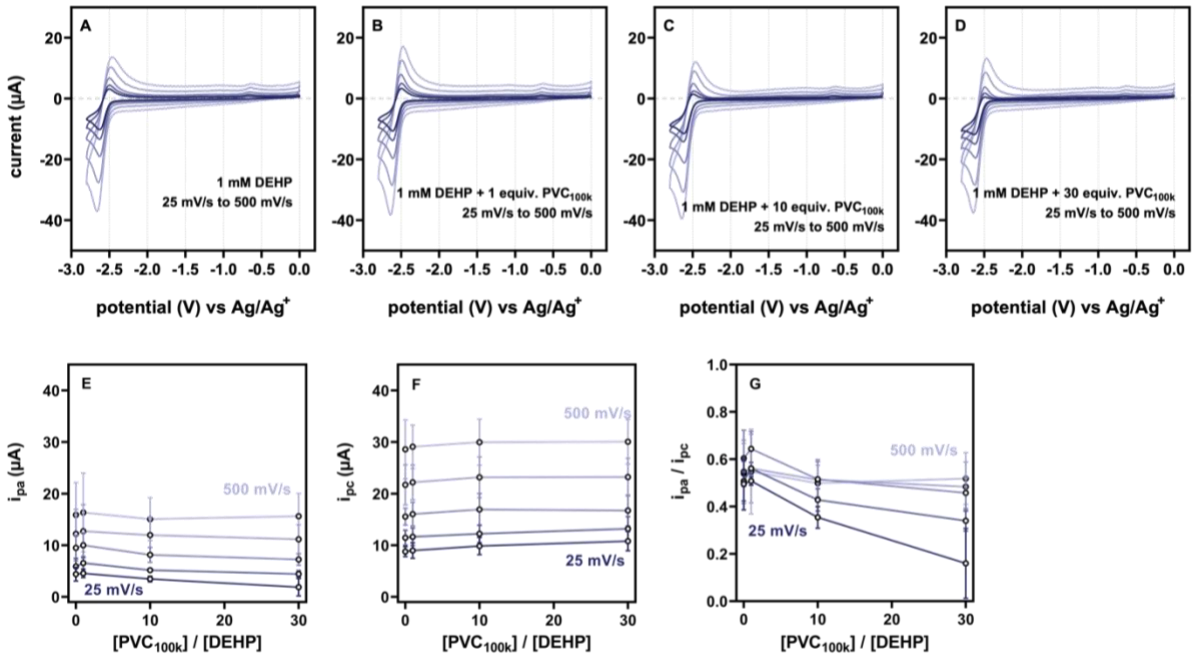


Figure S16. (A–D) Cyclic voltammetry of 1 mM DEHP in the presence of (A) 0 equiv. (B) 1 equiv. (C) 10 equiv. (D) 30 equiv. of PVC_{100k} with scan rates of 25, 50, 100, 250, 500 mV/s (darkest blue = 25 and lightest blue = 500 mV/s (E) oxidation current (F) reduction current (G) oxidation/reduction. The averages and standard deviations (represented by the error bars) can be found in Table S16.

Table S16. Raw data extracted from CV measurements, measured in triplicate using PVC_{35k} as the PVC source.

equiv. of PVC_{35k}	scan rate (mV/s)	i_{pa} (μA), oxidation					i_{pc} (μA), reduction					i_{pa} / i_{pc}				
		trial 1	trial 2	trial 3	avg.	std. dev.	trial 1	trial 2	trial 3	avg.	std. dev.	trial 1	trial 2	trial 3	avg.	std. dev.
0	25	5.0	2.9	5.4	4.4	1.34	9.6	7.7	9.1	8.8	0.97	0.52	0.37	0.59	0.50	0.11
	50	6.7	4.1	6.8	5.9	1.55	12.7	9.9	11.8	11.5	1.46	0.53	0.41	0.58	0.51	0.08
	100	10.7	5.9	9.8	9.5	2.49	17.3	13.4	15.6	15.5	1.63	0.62	0.44	0.63	0.60	0.12
	250	16.0	6.9	13.8	12.2	4.76	25.0	17.4	22.7	21.7	3.89	0.64	0.39	0.61	0.55	0.13
	500	20.3	8.7	18.6	15.9	6.26	33.3	22.2	30.3	28.6	5.71	0.61	0.39	0.62	0.54	0.13
1	25	5.0	7.3	5.1	5.8	1.28	10.0	12.1	9.5	10.6	1.38	0.50	0.60	0.54	0.54	0.05
	50	7.4	10.7	7.8	8.7	1.78	13.4	15.5	12.3	13.7	1.59	0.56	0.69	0.63	0.63	0.07
	100	12.8	16.0	11.9	13.1	1.96	18.3	22.1	16.2	18.2	2.81	0.70	0.72	0.74	0.72	0.02
	250	16.0	22.6	17.9	18.8	3.38	25.5	31.2	23.6	26.8	3.99	0.63	0.72	0.76	0.70	0.07
	500	26.3	30.3	25.2	27.3	2.73	36.0	41.4	30.7	36.0	5.32	0.73	0.73	0.82	0.76	0.05
10	25	3.8	4.8	4.3	4.3	0.50	12.0	13.0	10.1	11.7	1.47	0.31	0.37	0.42	0.37	0.06
	50	5.0	7.5	7.0	6.5	1.32	13.6	16.5	12.9	14.4	1.92	0.37	0.45	0.54	0.45	0.09
	100	10.1	12.3	10.5	10.7	1.06	19.0	21.6	17.0	18.9	1.96	0.53	0.57	0.62	0.57	0.04
	250	15.1	13.8	16.4	15.1	1.29	27.3	26.7	23.8	25.9	1.91	0.55	0.52	0.69	0.59	0.09
	500	19.6	17.3	23.0	20.0	2.84	34.5	33.3	32.0	33.2	1.26	0.57	0.52	0.72	0.60	0.10
30	25	0	0	0	0	0	15.4	18.0	10.0	14.5	4.10	0	0	0	0	0

	50	4.0	0	4.7	2.9	2.56	15.6	22.1	12.2	16.6	5.03	0.26	0	0.39	0.22	0.20
	100	8.5	9.6	8.0	8.3	1.03	19.4	28.2	15.9	19.6	6.07	0.44	0.34	0.50	0.44	0.07
	250	13.9	9.4	12.3	11.9	2.32	26.9	37.0	21.2	28.4	8.02	0.52	0.25	0.58	0.45	0.17
	500	19.1	11.4	17.0	15.9	3.99	34.6	42.2	27.1	34.6	7.56	0.55	0.27	0.63	0.48	0.19

Table S17. Raw data extracted from CV measurements, measured in triplicate using PVC_{47k} as the PVC source.

equiv. of PVC_{47k}	scan rate (mV/s)	i_{pa} (μA), oxidation					i_{pc} (μA), reduction					i_{pa} / i_{pc}				
		trial 1	trial 2	trial 3	avg.	std. dev.	trial 1	trial 2	trial 3	avg.	std. dev.	trial 1	trial 2	trial 3	avg.	std. dev.
1	25	3.6	5.8	4.7	4.7	1.10	9.9	9.4	8.1	9.1	0.92	0.36	0.62	0.58	0.52	0.14
	50	5.3	8.4	6.7	6.8	1.56	12.7	12.8	10.7	12.0	1.21	0.41	0.66	0.63	0.57	0.13
	100	8.0	11.8	10.1	10.0	1.89	17.0	17.1	14.2	16.1	1.68	0.47	0.69	0.71	0.63	0.13
	250	6.9	17.1	13.7	12.6	5.16	21.3	25.3	20.8	22.5	2.45	0.32	0.67	0.66	0.55	0.20
	500	9.1	21.7	18.3	16.3	6.52	26.6	34.4	27.5	29.5	4.25	0.34	0.63	0.66	0.55	0.18
10	25	3.1	3.8	3.2	3.4	0.38	10.6	8.7	8.2	9.2	1.24	0.29	0.44	0.39	0.37	0.07
	50	4.9	5.9	5.1	5.3	0.52	13.2	11.1	10.5	11.6	1.43	0.37	0.53	0.49	0.46	0.08
	100	7.7	9.4	7.4	8.2	1.07	17.2	14.8	13.8	15.3	1.73	0.45	0.64	0.54	0.54	0.09
	250	8.1	14.0	12.0	11.4	2.98	22.3	21.6	20.6	21.5	0.87	0.36	0.65	0.58	0.53	0.15
	500	10.3	18.6	15.9	14.9	4.26	28.1	28.3	28.0	28.1	0.14	0.37	0.66	0.57	0.53	0.15
30	25	0	0	0	0	0	11.7	9.2	10.0	10.3	1.30	0	0	0	0	0
	50	3.2	4.2	3.9	3.8	0.52	13.7	11.0	11.7	12.1	1.38	0.24	0.39	0.33	0.32	0.08
	100	5.2	7.2	6.0	6.1	1.04	17.3	14.1	15.4	15.6	1.62	0.30	0.51	0.39	0.40	0.11
	250	6.7	11.4	9.3	9.1	2.34	21.7	19.4	20.3	20.5	1.17	0.31	0.58	0.46	0.45	0.14
	500	8.8	15.5	12.3	12.2	3.38	27.1	25.6	26.6	26.4	0.78	0.32	0.61	0.46	0.46	0.14

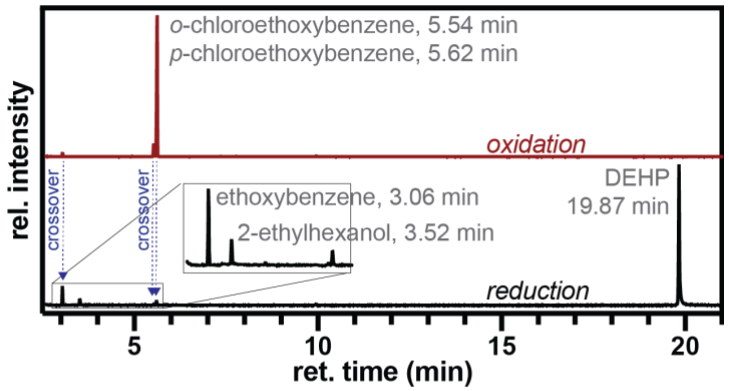
Table S18. Raw data extracted from CV measurements, measured in triplicate using PVC_{100k} as the PVC source.

equiv. of PVC_{100k}	scan rate (mV/s)	i_{pa} (μA), oxidation					i_{pc} (μA), reduction					i_{pa} / i_{pc}				
		trial 1	trial 2	trial 3	avg.	std. dev.	trial 1	trial 2	trial 3	avg.	std. dev.	trial 1	trial 2	trial 3	avg.	std. dev.
1	25	5.3	4.7	3.7	4.6	0.81	10.1	9.5	7.3	9.0	1.50	0.53	0.49	0.51	0.51	0.02
	50	7.6	6.9	5.2	6.6	1.24	12.9	12.4	9.7	11.6	1.72	0.59	0.56	0.53	0.56	0.03
	100	12.2	10.4	7.4	10.0	2.45	18.0	16.6	13.5	16.0	2.31	0.68	0.62	0.55	0.64	0.07
	250	18.6	10.2	9.3	12.7	5.14	25.6	22.2	18.8	22.2	3.39	0.73	0.46	0.49	0.56	0.15
	500	25.1	12.4	11.5	16.3	7.63	33.4	28.9	25.0	29.1	4.20	0.75	0.43	0.46	0.55	0.18
10	25	4.1	3.2	3.1	3.5	0.54	11.0	10.6	7.9	9.8	1.66	0.37	0.30	0.39	0.35	0.05
	50	5.5	5.1	4.9	5.2	0.29	13.4	13.0	10.3	12.2	1.70	0.41	0.39	0.48	0.43	0.05
	100	9.8	7.6	7.1	8.1	1.44	19.6	17.6	13.6	16.9	3.08	0.50	0.43	0.52	0.52	0.08
	250	16.0	9.5	10.5	12.0	3.51	27.4	22.6	19.5	23.2	3.97	0.58	0.42	0.54	0.51	0.09
	500	19.8	12.0	13.5	15.1	4.14	34.9	28.7	26.3	30.0	4.47	0.57	0.42	0.51	0.50	0.08
30	25	3.3	2.3	0	1.9	1.69	11.3	12.4	8.7	10.8	1.87	0.29	0.19	0	0.16	0.15
	50	5.1	4.4	3.8	4.4	0.66	14.0	15.0	10.5	13.2	2.37	0.37	0.29	0.36	0.34	0.04
	100	8.5	6.8	6.4	7.2	1.12	18.0	18.9	13.3	16.7	2.96	0.47	0.36	0.48	0.46	0.07
	250	14.4	9.1	10.0	11.2	2.81	25.6	25.0	19.0	23.2	3.64	0.56	0.36	0.52	0.48	0.10
	500	20.7	13.1	13.0	15.6	4.42	33.0	32.1	25.1	30.1	4.31	0.63	0.41	0.52	0.52	0.11

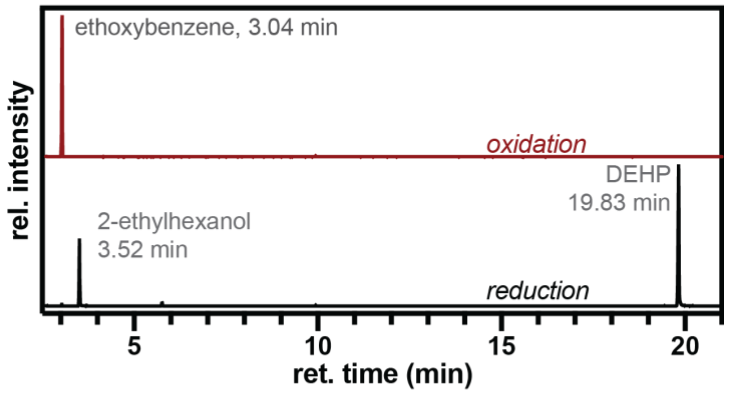
VI. Bulk electrolysis

Bulk electrolysis under constant current was performed to monitor the voltage readout of the reaction. After constant current bulk electrolysis, each half-reaction was analyzed by

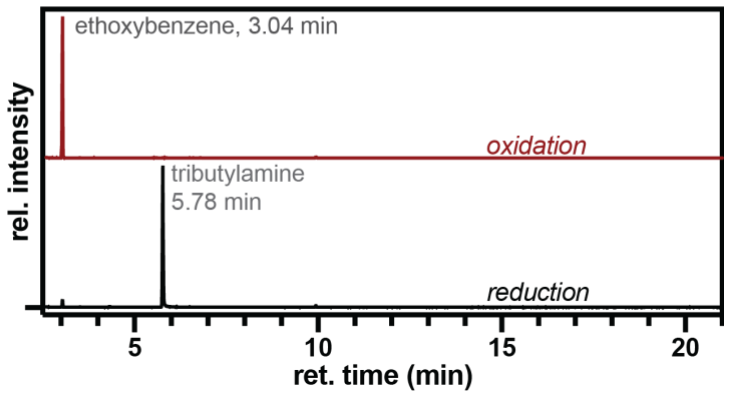
a) anodic cell: ethoxybenzene
cathodic cell: DEHP and PVC, **-5 mA ≈ -2.5 V**



b) anodic cell: ethoxybenzene
cathodic cell: DEHP only, **-5 mA ≈ -2.6 V**



c) anodic cell: ethoxybenzene
cathodic cell: PVC only, **-5 mA ≈ -3.5 V**



GC-MS. The voltages (vs. Ag/Ag^{+}) were read at capacity 0 mA*h, see Figure 3B in the manuscript.

Figure S17. GC-MS traces of each half-reaction after constant current bulk electrolysis.

The theoretical capacity of 5 mL of a 50 mM DEHP solution (0.25 mmol) was calculated to be 6.70 mA*h using the following conversion, in which 96485 C/mol is the Faraday constant.

$$0.25\ mmol\ DEHP * \frac{1\ mol}{1000\ mmol} * \frac{96485\ C}{1\ mol} * \frac{1\ A * s}{1\ C} * \frac{1000\ mA}{1\ A} * \frac{1\ h}{3600\ s} = 6.7\ mA * h$$

VII. Real plastics scenarios

Reaction with PVC_{solid}

This reaction was performed according to General Procedure C, using 0.20 g of PVC_{solid} (see page S5 for isolation procedure). The reaction was performed twice.

Reaction with PVC_{tubing}

This reaction was performed according to General Procedure C, using 0.30 g of PVC_{tubing} (~67% by wt PVC = ~0.20 g PVC_{solid}). A ~2 inch piece of tubing was cut up in half lengthwise and then cut into smaller pieces that were added to the reaction (photo below). The PVC_{tubing} pieces did not fully dissolve in the reaction mixture. The reaction was performed twice.

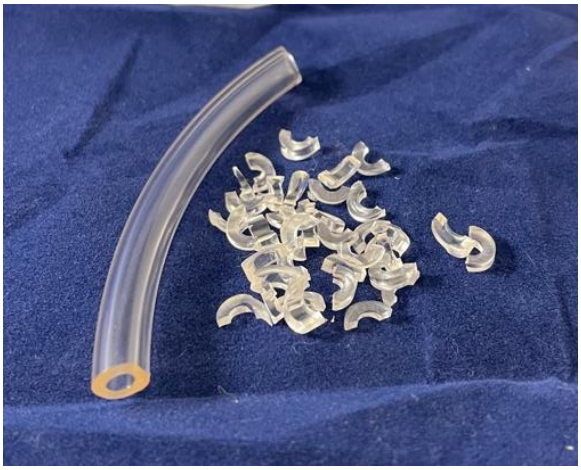


Figure S18. PVC_{tubing} and PVC_{tubing} cut up into smaller pieces.

Reaction with PVC_{tubing} and mixed plastics

This reaction was performed according to General Procedure C, using 0.30 g of PVC_{tubing} (~67% by wt PVC = ~0.20 g PVC_{solid}). Other plastics were collected from household items (water bottle, food container lids, medicine container, Styrofoam cup) and the polymer type was identified by the recycling code information listed on the item. Each plastic item cleaned with water, wiped dry, and cut into a small piece that was added into the reaction mixture. The reaction was performed once. The masses of each plastic piece were: 63 mg PET, 84 mg HDPE, 96 mg LDPE, 56 mg LLDPE, 80 mg PP, and 58 mg PS.

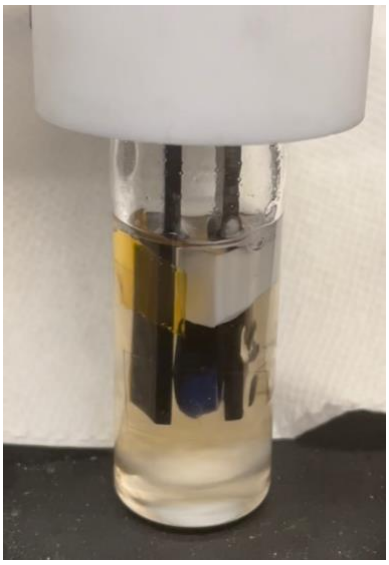


Figure S19. Reaction mixture containing PVC_{tubing} and pieces of mixed plastic items.

Table S19. Summary of data collected from reactions using real plastic items.

entry	**PVC** source	**possible contaminant(s)**	conversion of **1** (%)	consumption of **DEHP** (%)	yield of **2** (%)	NBu_3
1	PVC_{solid}	none	66	-	30	y
2	PVC_{solid}	none	55	-	33	y
3	PVC_{tubing}	none	85	95	62	n
4	PVC_{tubing}	none	89	91	64	n
5	PVC_{tubing}	mixed plastics	76	100	67	n

VIII. Characterization of dPVC after electrolysis

Isolation of dechlorinated PVC (dPVC) under standard conditions

After performing the electrolysis reaction according to General Procedure C, dPVC was recovered using the following protocol: The reaction mixture was poured into 200 mL methanol while stirring to precipitate the polymer. The polymer was collected by filtration and then redissolved in 5 mL THF. The solution was poured into 200 mL methanol while stirring to precipitate the polymer, again. The polymer was collected by filtration, and the dissolution and precipitation were repeated one more time. The polymer was collected by filtration and dried under vacuum overnight.

Figure S20. Photo of dPVC recovered from reactions performed using PVC_{47k} with 1 equiv. of DEHP ($dPVC_{DEHP}$, left) and with no DEHP ($dPVC_{alone}$, right).

Size-exclusion chromatography

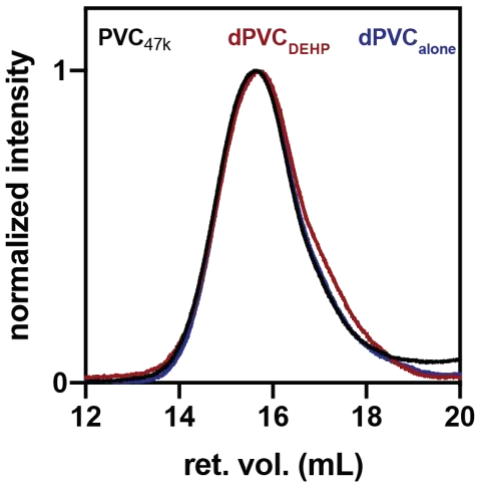


Figure S21. Normalized SEC traces of PVC and dPVC samples from standard conditions (RI detection). All samples were run in the same batch.

Elemental analysis

Elemental analysis indicated that both dPVC samples contained chlorinated repeat units, but dPVC recovered from reactions that include DEHP show a higher degree of dechlorination. An estimate of % dechlorination was calculated using the equation below.

$$\%\ dechlorination\ = \left(1 - \frac{\%\ Cl\ \text{dPVC}}{\%\ Cl\ \text{PVC}}\right) * 100\%$$

Table S20. Summary of elemental analysis data collected on PVC and dPVC recovered from reactions performed using PVC_{47k} with 1 equiv. of DEHP and with no DEHP.

element	mass %			
	PVC (theoretical)	**PVC (experimental)**	**dPVC, DEHP**	**dPVC, no DEHP**
C	38.44	38.7	46.0	39.0
H	4.84	5.0	5.8	4.9
N	0.00	0.0	0.0	0.0
Cl	56.72	56.5	43.5	53.4
total	100	100.2	95.3	97.3
approx. % dechlorination			***23.0 %***	***5.5%***

Thermogravimetric analysis (TGA)

TGA was used to estimate the relative amount of chlorine-containing repeat units in each dPVC sample. The thermal mass loss profile of PVC shows two major steps. The first step occurs at ~300 °C and generates mostly HCl along with some hydrocarbon degradation products.[2] The second step occurs at ~450 °C and degrades the remaining hydrocarbon content of the material. PVC_{47k} retains 36% of its mass after the first thermal step (64% mass loss). Samples of dPVC are expected to show less mass loss during the first stage because some HCl has already been removed from the polymer. This change in mass is observed. Recovered dPVC from reactions performed with DEHP retains 45% mass (55% mass loss), while dPVC recovered from reaction without DEHP retains 40% mass (60% mass loss). In both cases, less mass is lost from dPVC, further supporting that some HCl was emitted during electrolysis. This data suggests that more HCl was lost when DEHP was included in the reaction, which agrees with the higher chlorination yields observed under these conditions.

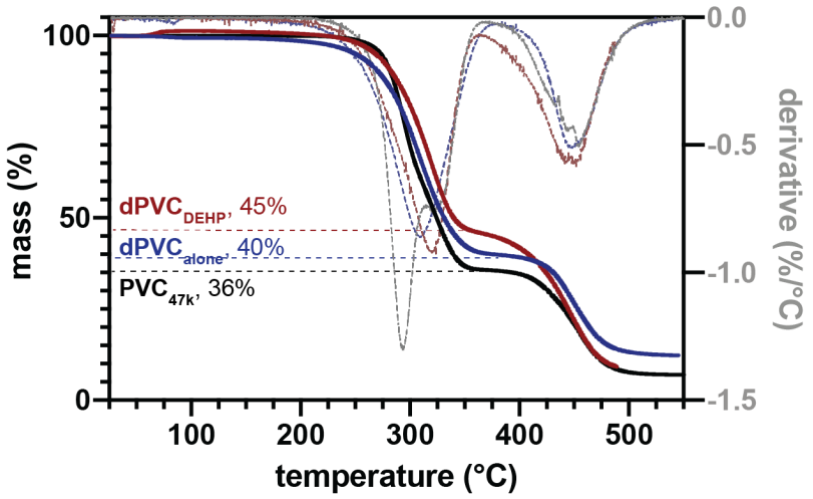


Figure S22. TGA mass loss profiles collected from PVC_{47k} (black) and dPVC recovered from reactions performed using PVC_{47k} with 1 equiv. of DEHP (red) and with no DEHP (blue). The % mass remaining after the first stage is indicated on the plot. The first derivative was used to identify the completion of the first mass loss stage, designated when the first derivative reached zero.

^{1}H NMR spectra

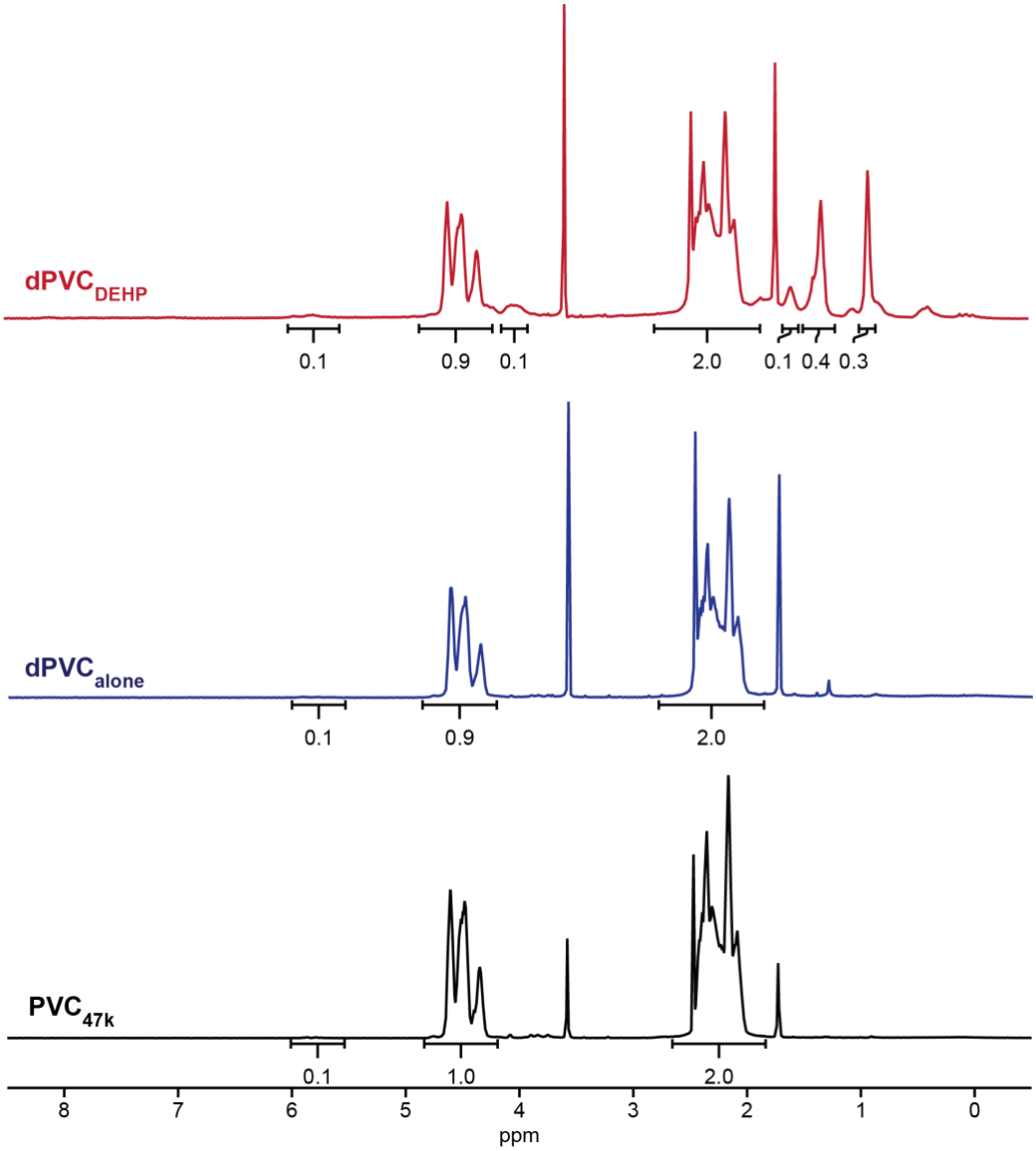


Figure S23. Stacked ^{1}H NMR spectra (500 MHz, THF-d_8) of dPVC recovered from reactions performed with DEHP (red —) and without DEHP (blue —) and PVC$_{47k}$ (black —).

Infrared spectroscopy (IR)

The IR spectrum of dPVC recovered from reactions performed with DEHP shows weak C_{sp3}–H stretching from 2850–2900 cm^{-1} and a strong carbonyl stretch at 1726 cm^{-1}, which may be from oxidation of the polymer backbone or from residual DEHP. Otherwise, the IR spectra of both dPVC samples do not vary qualitatively from PVC starting material, suggesting the polymer contains a significant portion of unreacted PVC repeat units.

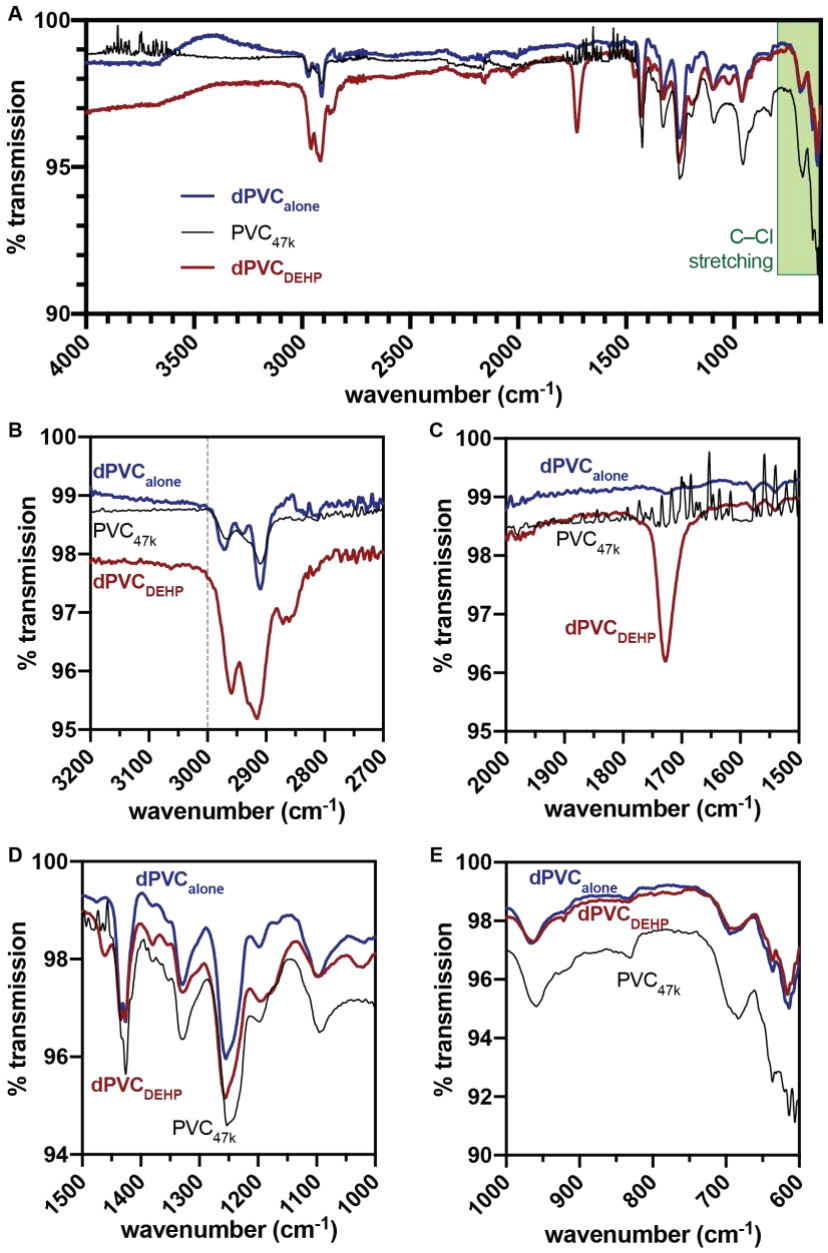


Figure S24. Full IR spectra of (A) PVC_{47k} (black —), dPVC recovered from reactions performed with DEHP (red —) and without DEHP (blue —) and (B–E) the same IR spectra zoomed into smaller wavenumber regions.

Differential scanning calorimetry (DSC)

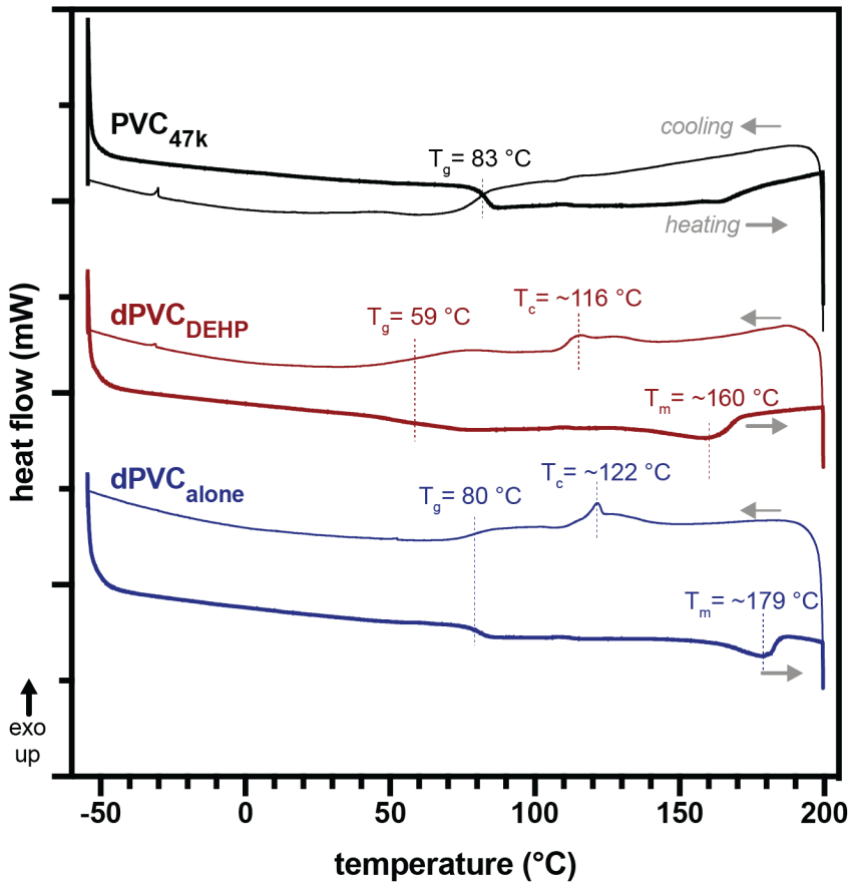


Figure S25. DSC thermograms of PVC_{47k} (black —), dPVC recovered from reactions performed with DEHP (red —) and without DEHP (blue —). The second heating/cooling cycle in shown.

Isolation of dechlorinated PVC (dPVC) under extended conditions

The electrolysis reaction using the following conditions using an undivided cell. PVC (200 mg, 3.2 mmol (repeat unit), 8.1 equiv. (repeat unit)), NBu_4BF_4 (264 mg, 0.80 mmol), dimethylphthalate (0.653 mL, 4.0 mmol, 10.0 equiv.), ethoxybenzene (0.510 mL, 0.4 mmol), tridecane internal standard (0.500 mL), and DMF (8 mL) were added to a 10 mL *ElectraSyn*® reaction vessel equipped with Teflon coated magnetic stir bar (egg-shaped, 16 mm length) and two graphite electrodes (0.8 x 0.2 x 5.20 cm). All reagents were dissolved by stirring for at least 15 min, then the reaction mixture was subjected to constant current electrolysis (30 mA) with alternating polarity (15 min) at rt. The reaction was stirred at 400 rpm for 24 h.

After electrolysis, dPVC was recovered using the following protocol. The reaction mixture was poured into 200 mL methanol while stirring to precipitate the polymer. The polymer was collected by filtration and then redissolved in 5 mL THF. The solution was poured into 200 mL methanol while stirring to precipitate the polymer, again. The polymer was collected by filtration, and the dissolution and precipitation processes were repeated one more time. The polymer was collected by filtration and dried under vacuum overnight.

Size-exclusion chromatography

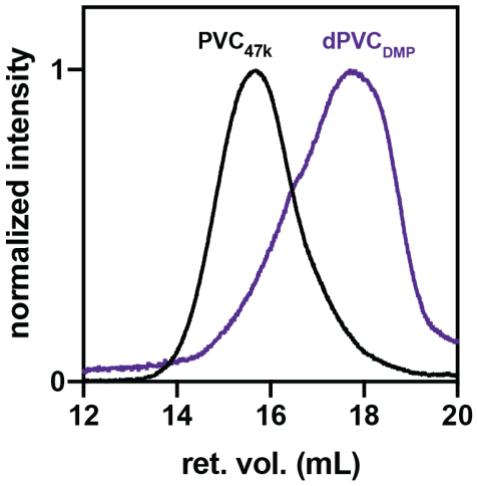


Figure S26. Normalized SEC traces of PVC and dPVC sample from extended conditions (RI detection). All samples were run in the same batch. Molar mass data for PVC_{47k}: M_n = 57 kg/mol, M_w = 123 kg/mol, $Đ_M$ = 2.14; $dPVC_{DMP}$: M_n = 14 kg/mol, M_w = 35 kg/mol, $Đ_M$ = 2.14. Note, these samples were run several months apart those listed in Table S1, after repairs were made to the instrument.

IX. Proposed mechanisms

Reductive dechlorination

The pH of the electrolysis reaction was monitored using pH strips. The electrolysis was performed following General Procedure C using PVC_{47k} and DEHP. The arene substrate was not included in the reaction, to remove effects of the arene chlorination on pH. The pH strips indicated that the reaction became more acidic during electrolysis. The change in pH is attributed to the degradation of PVC during electrolysis, likely releasing HCl.

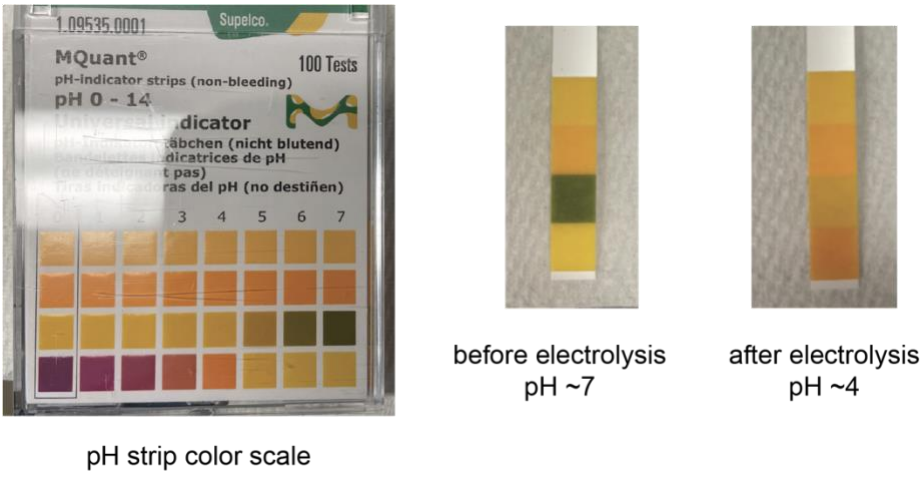


Figure S27. Photos of the pH strip color scale and pH strips immediately after being wetted with the reaction mixture.

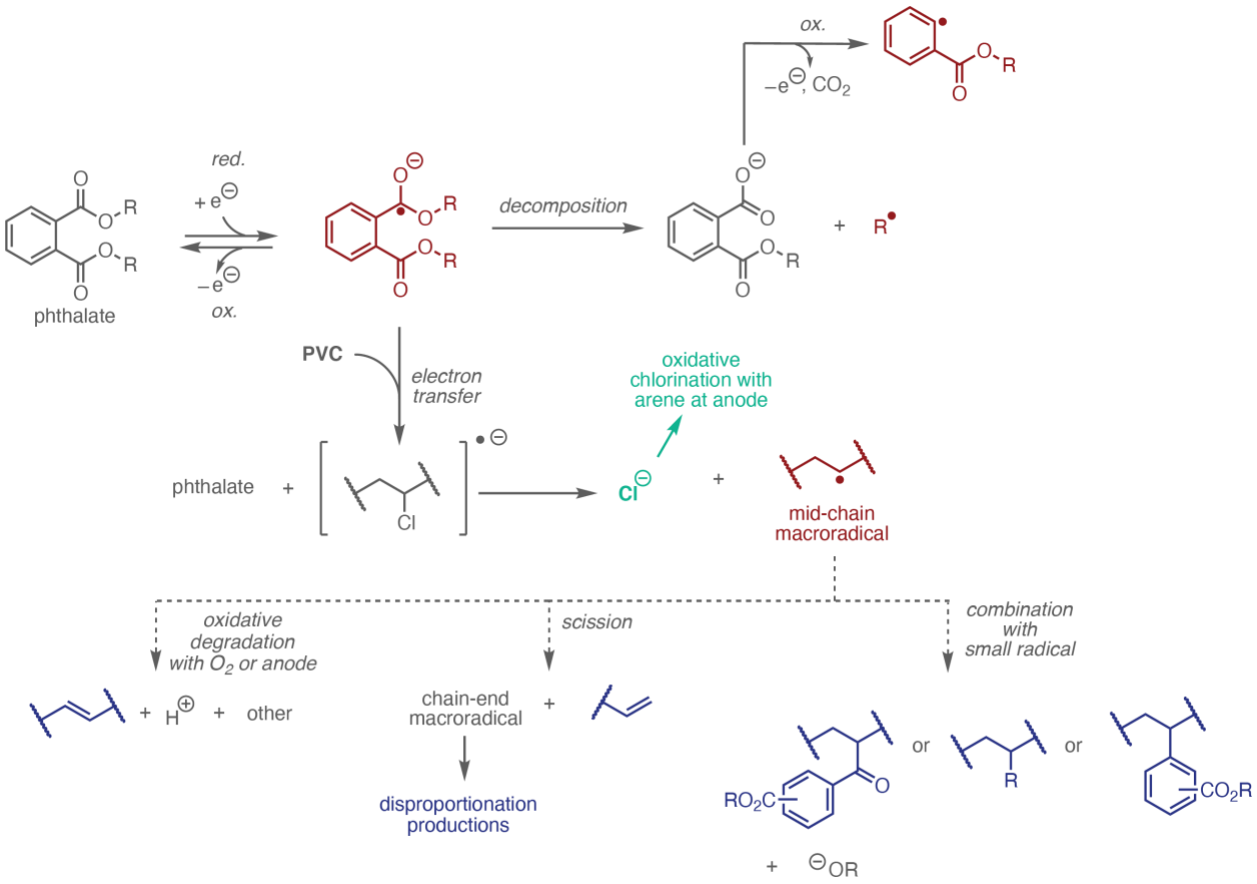


Figure S28. Proposed reductive dechlorination mechanism and macroradical reaction pathways.

Oxidative chlorination

Control reactions were performed to identify the possible chlorine species in solution. The chlorination reaction did not proceed when PVC was not included in the reaction (entry 2), supporting the role of PVC as the chloride source. The reaction proceeded cleanly when HCl was used as the chloride source (entry 3), supporting the notion that chloride ions are likely generated from PVC reduction. When TEMPO was added, no product was observed in the PVC/DEHP reaction (entry 4) nor the HCl control reaction (entry 5), suggesting that radical intermediates may be involved in the oxidative chlorination half-reaction, either to convert Cl^- into an active chloride species or in the arene chlorination step. The reaction proceeded with both NaOCl (entry 6) or Cl_2 (entry 7) as the chloride source without any electrical potential, suggesting that either hypochlorite or chlorine could be the active chloride species in this reaction. The fact that the PVC/DEHP reaction proceeds better open to air suggests that water may be generating hypochlorite (OCl^-) in situ. Taken together, this data supports the possible reaction pathway in which PVC is reductively degraded into HCl, and then Cl^- is converted into Cl_2 (or OCl^-), which reacts with arene **1** to generate product **2**.

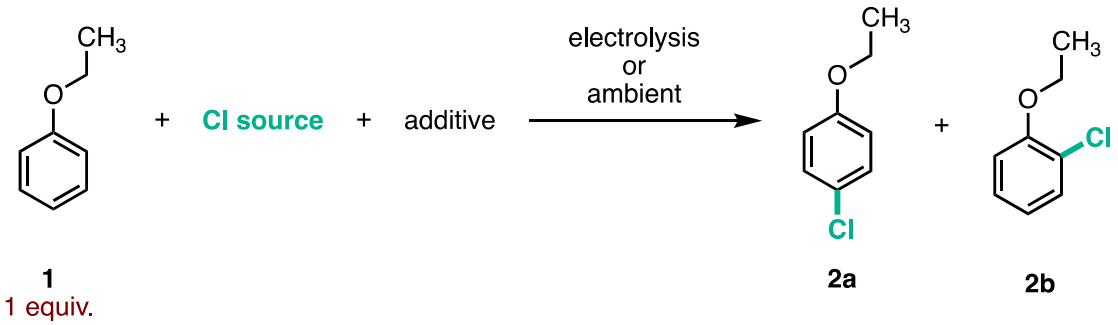


Table S21. Reactions performed to vary the possible chloride source.

entry	Cl source	additive	conditions	yield of **2** (%)
1	PVC_{47k} (8 equiv.)	DEHP (1 equiv.)	electrolysis[a]	85%
2	none	DEHP (1 equiv.)	electrolysis[a]	0%
3	HCl (3.2 equiv.)[b]	none	electrolysis[a]	quant.
4	PVC_{47k} (8 equiv.)	DEHP (1 equiv.), TEMPO (3.5 equiv.)[c]	electrolysis[a]	0%
5	HCl (3.2 equiv.)[b]	TEMPO (3.5 equiv.)[c]	electrolysis[a]	0%
6	NaOCl (3.2 equiv.)	none	ambient[d]	33%
7	Cl_2 (excess)	none	ambient[e]	quant.

[a] Electrolysis conditions: performed according to General Procedure C.
[b] Concentrated HCl (37 %w/w, 0.100 mL, 1.3 mmol) was used in place of PVC and DEHP and added to the reaction after dilution with DMF.
[c] (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl (TEMPO, 0.219 g, 1.4 mmol) was added to the to the reaction before electrolysis.
[d] Ethoxybenzene (0.051 mL, 0.4 mmol) and tridecane (0.050 mL) were dispensed in a 20 mL vial and dissolved in DMF (6 mL). NaOCl solution (2.21 mL, 4.00–4.99% active chlorine) was added and the reaction stirred at rt for 16 h.
[e] Ethoxybenzene (0.051 mL, 0.4 mmol) and tridecane (0.050 mL) were dispensed in a 25 mL round bottom flask and dissolved in DMF (8 mL). Cl_2 was slowly bubbled into the solution and stirred at rt for 5 min. Cl_2 was produced by slowly adding concentrated HCl (2 mL) to a 12.5% NaOCl solution (20 mL).

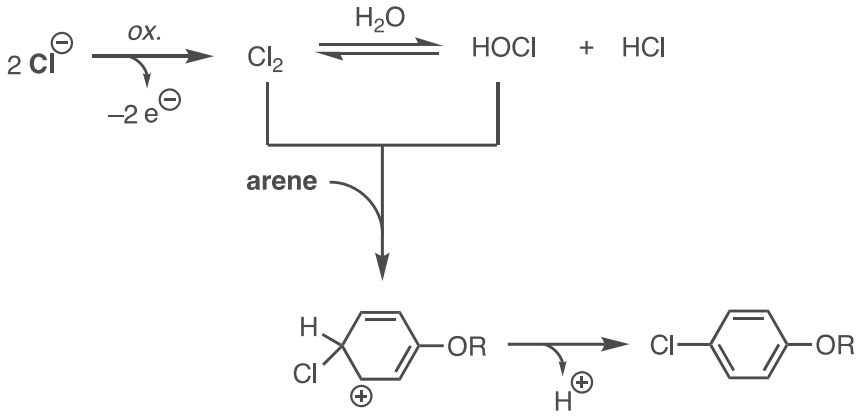
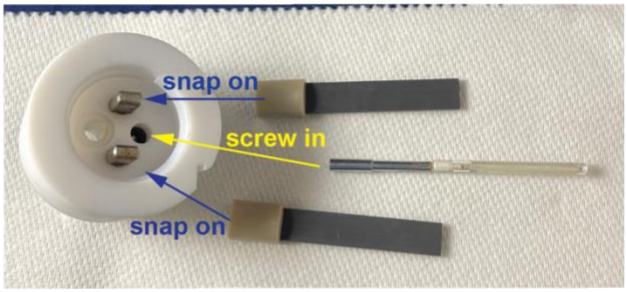


Figure S29. Proposed oxidative arene chlorination mechanism.

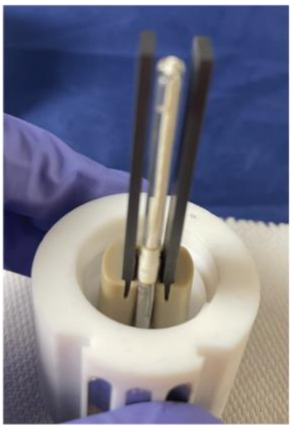
X. ElectraSyn setup guide

Undivided cell

step 1: Equip ElectraSyn® cap with graphite electrodes and reference electrode (optional*).



disassembled ElectraSyn® cap, graphite electrodes, and Ag wire reference electrode in 3 M KCl (bottom of cap shown)



graphite electrodes plugged into W and C electrode positions and reference electrode screwed in on ElectraSyn® cap

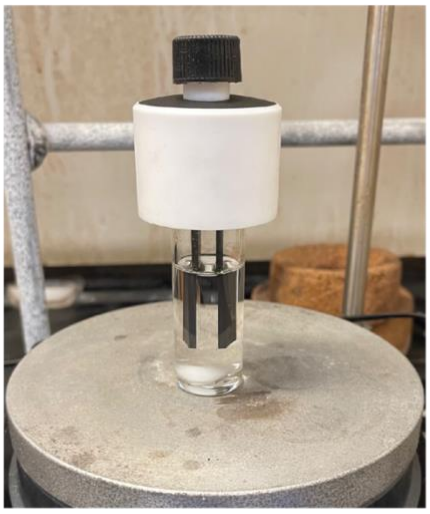
* reference electrode was not used in constant current reactions

step 2: Measure required amounts of each reagent and dispense into 10 mL ElectraSyn® vial.

chemical reagents used in reaction

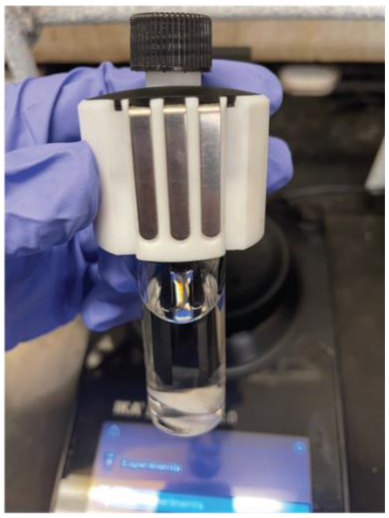
reagents added to 10 mL vial

step 3: Add stir bar and dispense DMF into the vial and then screw on ElectraSyn® cap. Stir reaction solution until for 15 min, until fully dissolved.

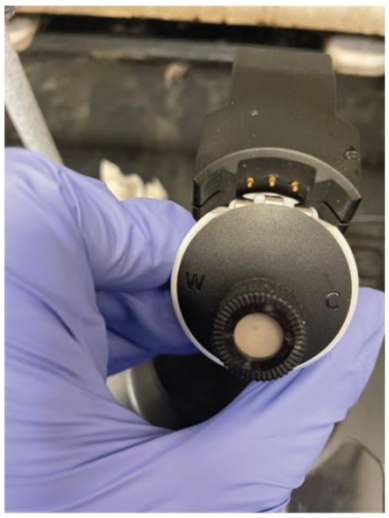


reaction after stirring for 15 minutes
(front of cap shown)

step 4: Connect vial+cap to the ElectraSyn® potentiostat.



connection ports on ElectraSyn® cap
(back of cap shown)



connecting cap to potentiostat

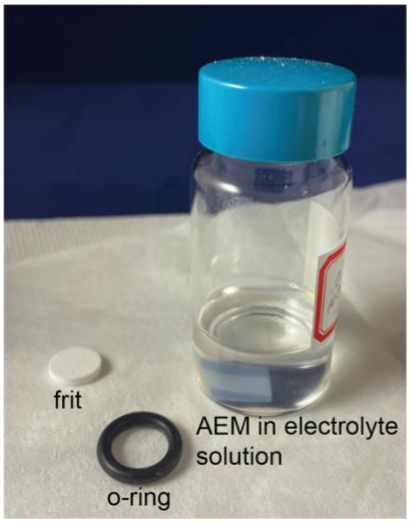
step 5: Configure settings and start reaction.

"ready-to-run" reaction setup

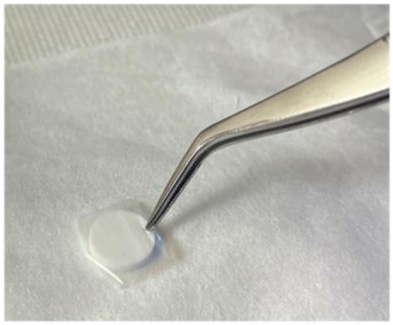
example of settings:
constant current
10 mA
no reference electrode
0.4 mmol substrate
total reaction time of 16 h
alternate current every 15 min
stir at 400 rpm

Divided cell

step 1: Gently place pre-soaked AEM on frit and secure with o-ring.



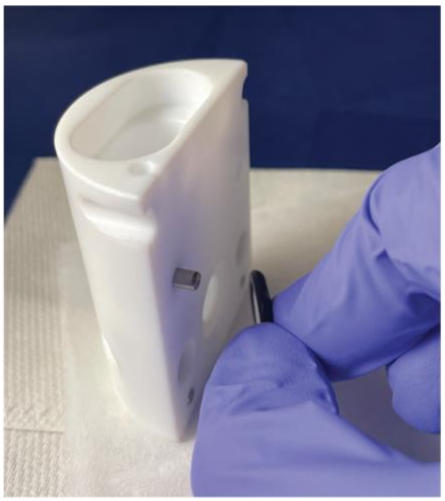
AEM = anion exchange membrane



placing AEM on top of frit

secure o-ring around frit to hold AEM in place

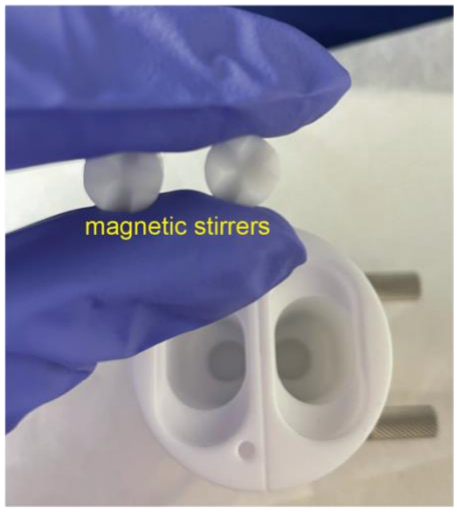
step 2: Assemble IKA Pro-Divide cell.



place the frit on the half-cell, the AEM should face the half-cell that will contain the polymer solution to avoid polymer clogging the frit

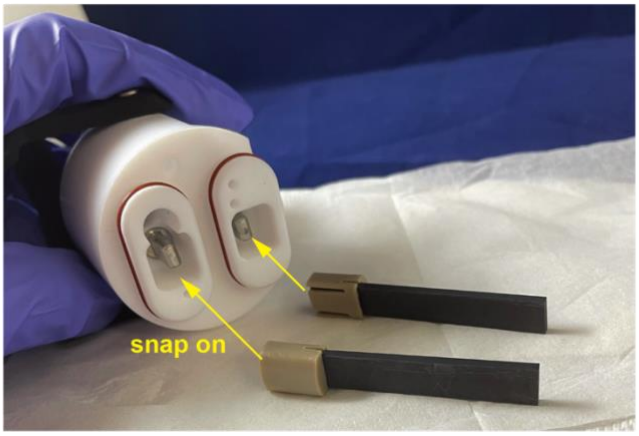
align both half-cells around frit

rotate thumb screws as tight as possible



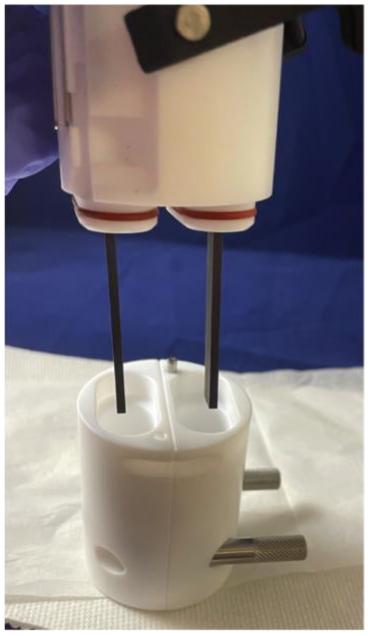
place a magnet stirrer in each half-cell

step 3: Assemble IKA Pro-Divide cap with electrodes.



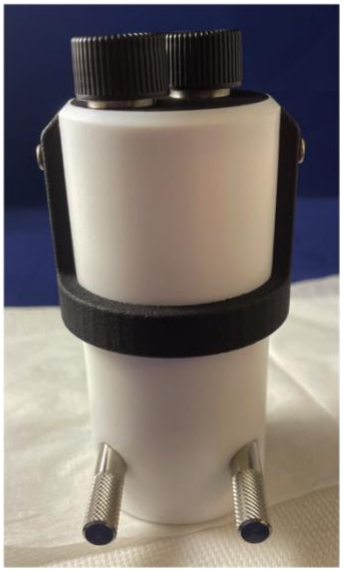
disassembled Pro-Divide cap and graphite electrodes (bottom of cap shown)

step 4: Add reagents and secure cap on a cell.



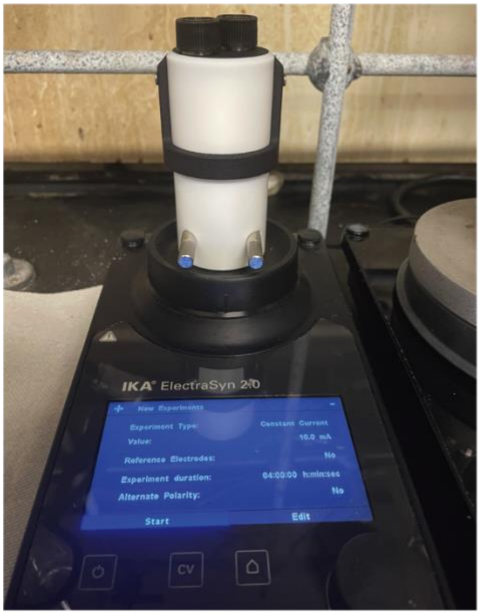
add reagents (not shown) and Pro-Divide cap with electrodes

connect cap to cell but clamping down the latch



assembled reaction vessel

step 5: Connect Pro-Divide to ElectraSyn® potentiostat, configure settings, and start reaction.



"ready-to-run" reaction setup

<u>example of settings:</u>
constant current
10 mA
no reference electrode
0.5 mmol substrate
total reaction time of 4 h
no alternating current
stir at 700 rpm

XI. Life cycle assessment

Functional Unit: 1 kg of chloroethoxybenzene (**2**)
Scope: Process Flow Diagrams

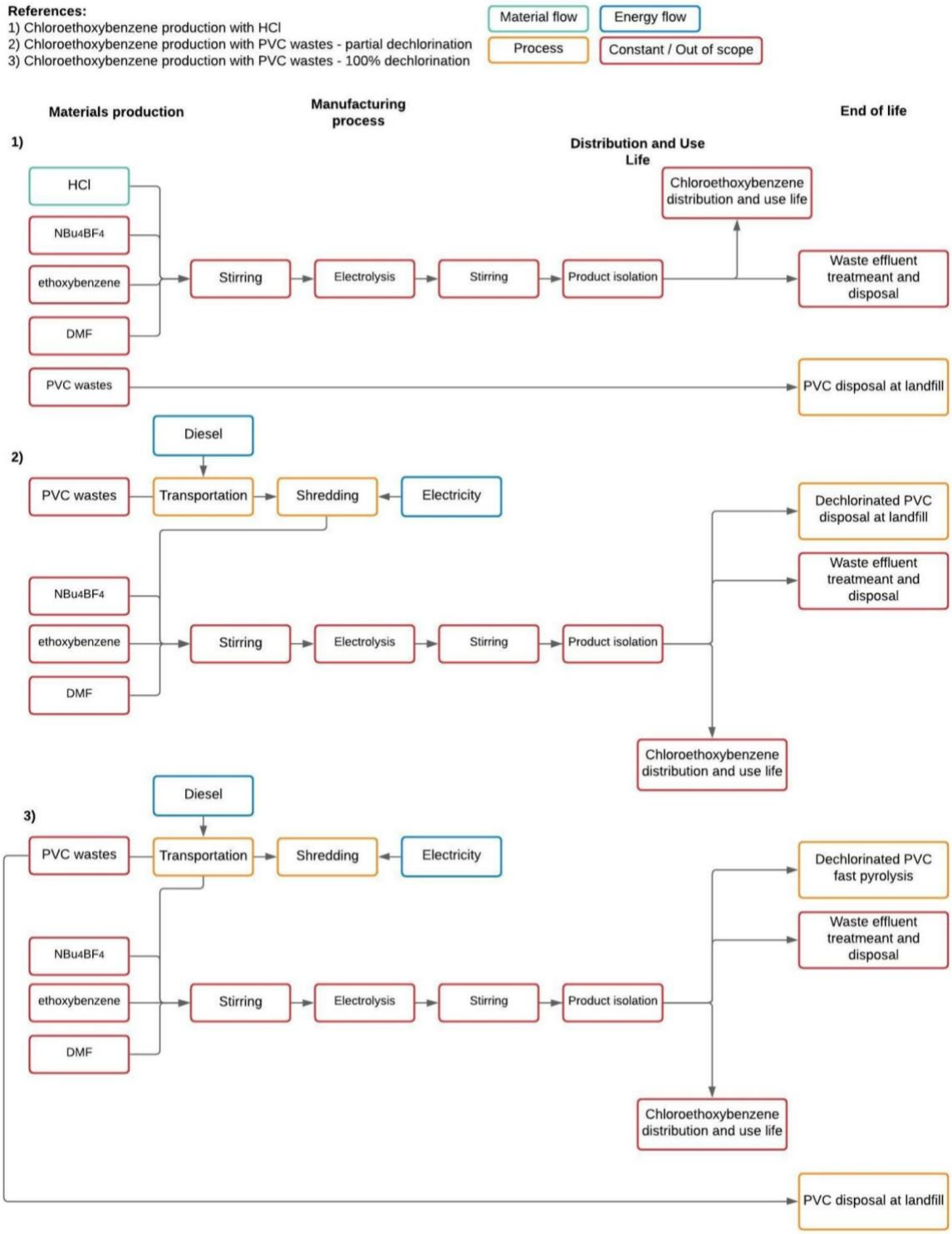


Figure S30. Process flow diagram of each scenario studied by life cycle assessment.

Assumptions:

- PVC production is left out of scope, because it is waste and therefore produced independently from this process.
- PVC wastes acquisition supply chain is assumed to be 100 km of transportation and shredding.
- Shredding process consumes 0.085 MJ/kg.[3]
- Because General Procedure C was followed for HCl and PVC reaction, the following items are considered to be constant, and are thus left out of scope:
    - repeated reagents
    - energy consumption during product synthesis and isolation
    - equipment required
    - electrode change/discard frequency
- PVC weight change with dechlorination is negligible.
- Use life of chloroethoxybenzene (**2**) is constant, and are thus left out of scope.
- PVC and partially dechlorinated PVC have the same impact when sent to landfill.
- Waste effluents are assumed to undergo the same treatment in any case, thus are left out of scope.
- Total impact of chemical recycling of plastics via pyrolysis: 0.739 kg CO_2 eq per kg of plastics (including displaced fossil fuels with the resulting products).[4]
- The disposal of a fixed amount of PVC wastes equivalent to the amount of PVC wastes required to produce 1 kg of chloroethoxybenzene (**2**) in scenario 2, is considered for all scenarios.

Table S22. Life cycle inventories used with each scenario.

Item	Units	Scenario 1	Scenario 2	Scenario 3
Materials Production				
HCl	kg	0.740	0	0
PVC wastes supply chain	tkm	0	0.373	0.040
PVC shredding	kWh	0	0.088	0.009
End of Life				
PVC to landfill	kg	3.732	3.732	3.335
Chemical recycling of dechlorinated PVC	kg	0	0	0.397

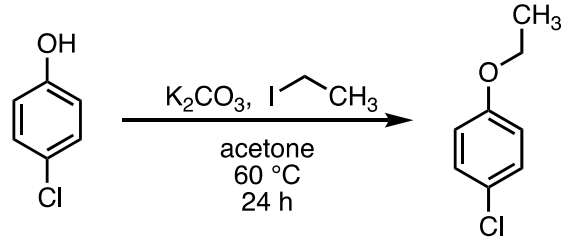
Table S23. Life cycle impact assessments. CO_2 equivalents are per unit of item listed.

Item	SimaPro: Ecoinvent library	SimaPro: Method	Units	Impact
Materials Production				
HCl	*Hydrochloric acid, from the reaction of hydrogen with chlorine, at plant/RER S*	*IPCC 2013 gwp 100a*	kg CO_2 eq/kg	1.320
PVC wastes supply chain	*Transport, combination truck, long-haul, diesel powered/tkm/RNA*	*IPCC 2013 gwp 100a*	kg CO_2 eq/tkm	0.0965
PVC shredding	*Electricity, high voltage {US}| market for electricity, high voltage | Cut-off, S*	*IPCC 2013 gwp 100a*	kg CO_2 eq/kWh	0.557
End of Life				
PVC to landfill	*Municipal Solid Waste (waste scenario) (RoW)*	*IPCC 2013 gwp 100a*	kg CO_2 eq/kg	0.074
Chemical recycling of dechlorinated PVC	*Values sourced from Jeswani et al., 2021[4]		kg CO_2 eq/kg	0.739

Table S24. Results of the life cycle impact assessment (LCIA) of global warming potential (GWP) for each scenario. CO_2 equivalents are per kg of chloroethoxybenzene (**2**).

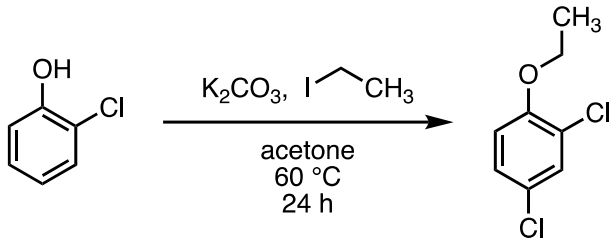
	Units	Scenario 1	Scenario 2	Scenario 3
LCIA - GWP	kg CO_2 eq	1.252	0.360	0.548

XII. Synthetic procedures



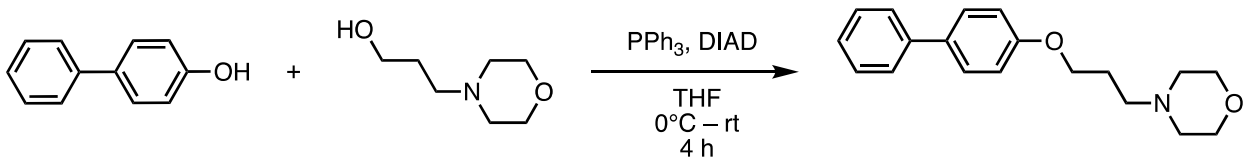
2a

4-chloro-1-ethoxybenzene (2a). Potassium carbonate (2.57g, 18.6 mmol, 1.2 equiv.) and 4-chlorophenol (1.99 g, 15.5 mmol, 1.0 equiv.) were added to a 50 mL round-bottom flask equipped with reflux condenser and dissolved in acetone (30 mL). Ethyl iodide (1.49 mL, 18.6 mmol, 1.2 equiv.) was added and the resulting solution was stirred at 60 °C. After 24 h, the reaction was cooled to rt and concentrated under reduced pressure. The crude reaction mixture was directly purified by silica gel column chromatography (0–100% ethyl acetate in hexanes) to obtain a viscous, colorless oil (2.01 g, 83%). NMR data is reported in Figure S33. HRMS (APCI+) calc'd for $C_9H_{10}ClO$ [M+H$^+$]: 157.0415; found: 157.0423.



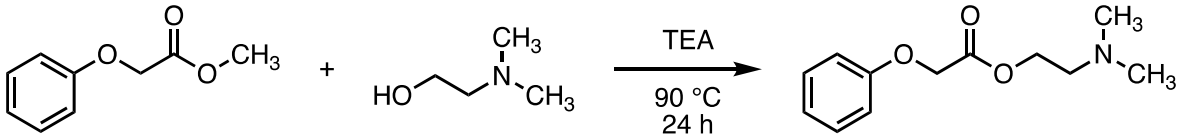
2b

2-chloro-1-ethoxybenzene (2b). Potassium carbonate (2.57g, 18.6 mmol, 1.2 equiv.) and 2-chlorophenol (1.99 g, 15.5 mmol, 1.0 equiv.) were added to a 50 mL round-bottom flask equipped with reflux condenser and dissolved in acetone (30 mL). Ethyl iodide (1.49 mL, 18.6 mmol, 1.2 equiv.) was added and the resulting solution was stirred at 60 °C. After 24 h, the reaction was cooled to rt and concentrated under reduced pressure. The crude reaction mixture was directly purified by silica gel column chromatography (0–100% ethyl acetate in hexanes) to obtain and viscous, colorless oil (1.85 g, 76%). NMR data is reported in Figure S34. HRMS (APCI+) calc'd for $C_9H_{10}ClO$ [M+H$^+$]: 157.0415; found: 157.0424.



4-(3-([1,1'-biphenyl]-4-yloxy)propyl)morpholine. 4-Phenylphenol (1.00 g, 5.88 mmol), triphenylphosphine (1.85 g, 7.05 mmol), and 4-(3-hydroxypropyl)morpholine (0.975 mL, 7.05 mmol) were added to a round-bottom flask under N_2 and dissolved in anhydrous

THF (17 mL). The reaction was cooled to 0 °C in an ice-bath and then diisopropyl azodicarboxylate (1.38 mL, 7.05 mmol) was added dropwise. The reaction was warmed for room temperature and stirred for a total of 4 h. After the reaction was complete, 50 mL of H_2O was added and then extracted 3 x 100 mL ethyl acetate. The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude material was further purified by silica gel column chromatography (0–80% (ethyl acetate + 5% triethylamine) in hexanes) to obtain a white solid (0.714 g, 2.40 mmol, 41%). NMR data is reported in Figure S35. HRMS (EI+) calc'd for $C_{19}H_{23}NO_2$ [M^+]: 297.1729; found: 297.1726.

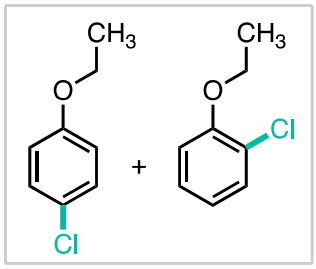


2-(dimethylamino)ethyl 2-phenoxyacetate. Methyl phenoxyacetate (1.00 mL, 1.15 g, 6.91 mmol), *N*,*N*-dimethylethanol amine (1.04 mL, 0.924 g, 10.4 mmol), and triethylamine (1 mL) were dispensed into an 8 mL glass vial. The reaction was stirred at 90 °C for 24 h. The crude reaction mixture was cooled to rt and directly purified by silicia gel chromatography (0–50% (ethyl acetate + 5% triethylamine) in hexanes) to obtain a colorless oil (1.23 g, 5.53 mmol, 80%). NMR data is reported in Figure S36. HRMS (EI+) calc'd for $C_{12}H_{17}NO_3$ [M^+]: 223.1208; found: 223.1212.

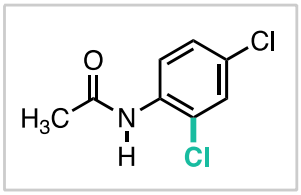
General Procedure E (divided cell paired electrolysis, constant current)

The *ElectraSyn® Pro-Divide* reaction vessel was assembled using graphite electrodes (0.8 x 0.2 x 5.20 cm) and a 5 micron frit separator layered with a PiperION anion-exchange membrane (pre-soaked in 0.1 M NBu_4BF_4 in DMF). The aromatic substrate (0.5 mmol), NBu_4BF_4 (231 mg, 0.70 mmol), and DMF (7 mL) were added to the working (anodic) chamber. PVC_{47k} (200 mg, 3.2 mmol (repeat unit), 6.4 equiv. (repeat unit)), NBu_4BF_4 (231 g, 0.70 mmol), DEHP (0.20 mL, 0.50 mmol, 1.0 equiv.), and DMF (7 mL) were added to the counter (cathodic) chamber. All reagents were added under air and then dissolved by stirring for at least 15 min. Then the reaction mixture was subjected to constant current electrolysis (10 mA) at rt. The anodic reaction was monitored by GC and stirred until all the aromatic substrate was consumed. The working (anodic) chamber was poured into ~250 mL of ethyl acetate and washed with H_2O (5 × 40 mL) and brine (1 × 50 mL) to remove DMF. The organic layer was dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude reaction was further purified by column chromatography and the final product dried under reduced pressure.

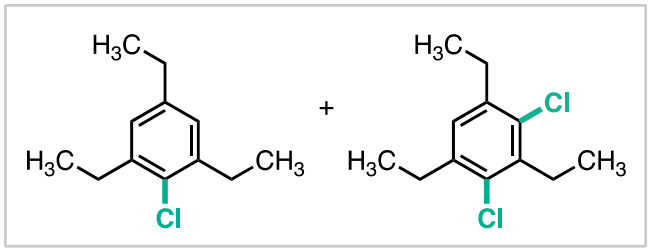
chloro-1-ethoxybenzene (2). 1-Ethoxybenzene (63 μL, 61 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 8 h. The crude product was purified by chromatography (mobile phase: 100% hexanes) to obtain a colorless oil (41 mg, 52% yield). NMR analysis indicated that the product was formed as a 4:1 mixture of regioisomers (4-chloro-1-ethoxybenzene: 2-chloro-1-ethoxybenzene). NMR data is reported in Figure S37. HRMS (APCI+) calc'd for $C_9H_{10}ClO$ [M+H$^+$]: 157.0415; found: 157.0422.



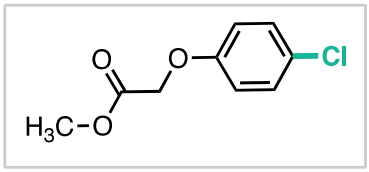
***N*-(2,4-dichlorophenyl)acetamide (3)**. *N*-(4-chlorophenyl)acetamide (85 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 10 h. The crude product was purified by chromatography (mobile phase: 0–100% gradient ethyl acetate in hexanes) to obtain an off-white solid (69 mg, 67% yield). NMR data is reported in Figure S38. HRMS (APCI+) calc'd for $C_8H_8Cl_2NO$ [M+H$^+$]: 203.9977; found: 203.9984.



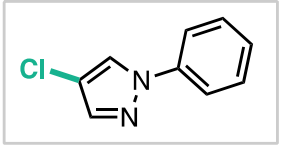
chloro-1,3,5-triethylbenzene (4). 1,3,5-Triethylbenzene (94 μL, 81 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 8 h. The crude product was purified by chromatography (mobile phase: 100% hexanes) to obtain a colorless liquid (77 mg, 76% yield). NMR analysis indicated that the product was formed as a 5:1 mixture of products (2-chloro-1,3-5-triethylbenzene: 2,4-dichloro-1,3,5-triethylbenzene). NMR data is reported in Figure S39. HRMS (EI+) calc'd for $C_{12}H_{17}Cl$: 196.1019 [M$^+$]; found: 196.1022; calc'd for $C_{12}H_{16}Cl_2$ [M$^+$]: 230.0629; found: 230.0629.



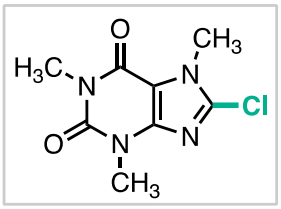
methyl 2-(4-chlorophenoxy)acetate (5). Methyl phenoxy acetate (72 μL, 83 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 7 h. The crude product was purified by chromatography (mobile phase: 15% ethyl acetate in hexanes) to obtain a yellow oil (72 mg, 72% yield). NMR data is reported in Figure S40. HRMS (APCI+) calc'd for $C_9H_{10}ClO_3$ [M+H$^+$]: 201.0313; found: 201.0322.



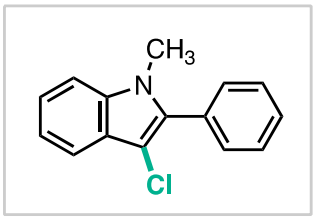
4-chloro-1-phenyl-1*H*-pyrazole (6). 1-Phenyl-1*H*-pyrazole (66 μL, 72 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 8 h. The crude product was purified by chromatography (mobile phase: 0–30% gradient ethyl acetate in hexanes) to obtain an off-white solid (64 mg, 71% yield). NMR data is reported in Figure S41. HRMS (EI+) calc'd for $C_9H_7ClN_2$ [M$^+$]: 178.0298; found: 178.0300.



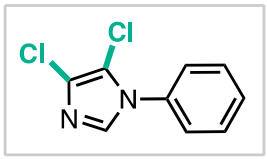
8-chloro-1,3,7-trimethyl-3,7-dihydro-1*H*-purine-2,6-dione (7). Caffeine (97 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 8 h. The crude product was purified by chromatography (mobile phase: 0–50% ethyl acetate in hexanes) to obtain a white solid (41 mg, 36% yield). NMR data is reported in Figure S42. HRMS (APCI+) calc'd for $C_8H_{10}ClN_4O_2$ [M+H$^+$]: 229.0487; found: 229.0482.



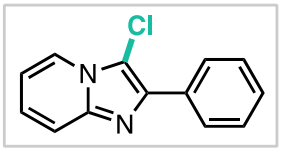
3-chloro-1-methyl-2-phenyl-1*H*-indole (8). 1-Methyl-2-phenyl-1*H*-indole (104 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 4 h. The crude product was purified by chromatography (mobile phase: 100% hexanes) to obtain a white solid (6.1 mg, 5% yield). NMR data is reported in Figure S43. HRMS (EI+) calc'd for $C_{15}H_{12}ClN$ [M$^+$]: 241.0658; found: 241.0664.



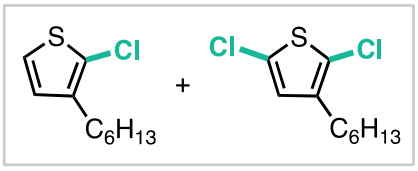
4,5-dichloro-1-phenyl-1*H*-imidazole (9). 1-Phenyl-1*H*-imidazole (63 μL, 72 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 4 hours. The crude product was purified by chromatography (mobile phase: 0–100% gradient ethyl acetate in hexanes) to obtain a white solid (14 mg, 13% yield). NMR data is reported in Figure S44. HRMS (EI+) calc'd for $C_9H_6Cl_2N_2$ [M$^+$]: 211.9908; found: 211.9907.



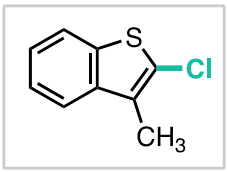
3-chloro-2-phenylimidazo[1,2-*a*]pyridine (10). 2-Phenylimidazo[1,2-*a*]pyridine (97 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 4 h. The crude product was purified by chromatography (mobile phase: 0–100% gradient ethyl acetate in hexanes) to obtain an off-white solid (27 mg, 24% yield). NMR data is reported in Figure S45. HRMS (APCI+) calc'd for $C_{13}H_{10}ClN_2$ [M+H$^+$]: 229.0527; found: 229.0526.



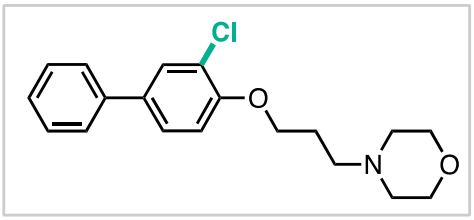
chloro-3-hexylthiophene (11). 3-Hexylthiophene (89 μL, 84 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 8 h. The crude product was purified by chromatography (mobile phase: 100% hexanes) to obtain a colorless oil (37 mg, 33% yield). NMR analysis indicated that the product was formed as a 1:1.8 mixture of products (2-chloro-3-hexylthiophene: 2,5-dichloro-3-hexylthiophene). NMR data is reported in Figure S46. HRMS (APCI+) calc'd for $C_{10}H_{16}ClS$ [M+H$^+$]: 203.0656; found: 203.0655; $C_{10}H_{15}Cl_2S$ [M+H$^+$]: 237.0266; found: 237.0263.



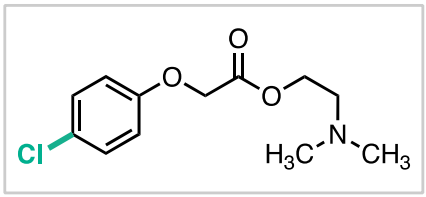
2-chloro-3-methylbenzo[*b*]thiophene (12). 3-Methylbenzo[*b*]thiophene (67 μL, 74 mg, 0.50 mmol) was reacted according to General Procedure E for a total of 10 h. The crude product was purified by chromatography (mobile phase: 100% hexanes) to obtain a colorless oil (50 mg, 55 % yield. NMR data is reported in Figure S47. HRMS (EI+) calc'd for C_9H_7ClS [M^+]: 181.9957; found: 181.9888.



4-(3-((3-chloro-[1,1'-biphenyl]-4-yl)oxy)propyl)morpholine (13). 4-(3-([1,1'-Biphenyl]-4-yloxy)propyl)morpholine (0.149 g, 0.50 mmol) was reacted according to General Procedure E for a total of 8 h. The crude product was purified by chromatography (mobile phase: 0–80% (ethyl acetate + 5% triethylamine)) to obtain and off-white solid (73 mg, 44% yield). NMR data is reported in Figure S48. HRMS (EI+) calc'd for $C_{19}H_{22}ClNO_2$ [M^+]: 331.1339; found: 331.1336.



2-(dimethylamino)ethyl 2-(4-chlorophenoxy)acetate (14). 2-(Dimethylamino)ethyl 2-phenoxyacetate (107 μL, 0.112 g, 0.5 mmol) was reacted according to General Procedure E for a total of 8 h. The crude product was purified by chromatography (mobile phase: 0–60% (ethyl acetate + 5% triethylamine)) to obtain a yellow oil (44 mg, 29% yield). NMR analysis indicated that the obtained oil contained 1:0.2 mixture of product and unreacted starting material, which were not separated chromatographically. NMR data is reported in Figure S49. HRMS (ESI+) calc'd for $C_{12}H_{17}ClNO_3$ [$M+H^+$]: 258.0891; found: 258.0894.



XIII. ^{1}H and ^{13}C NMR spectra

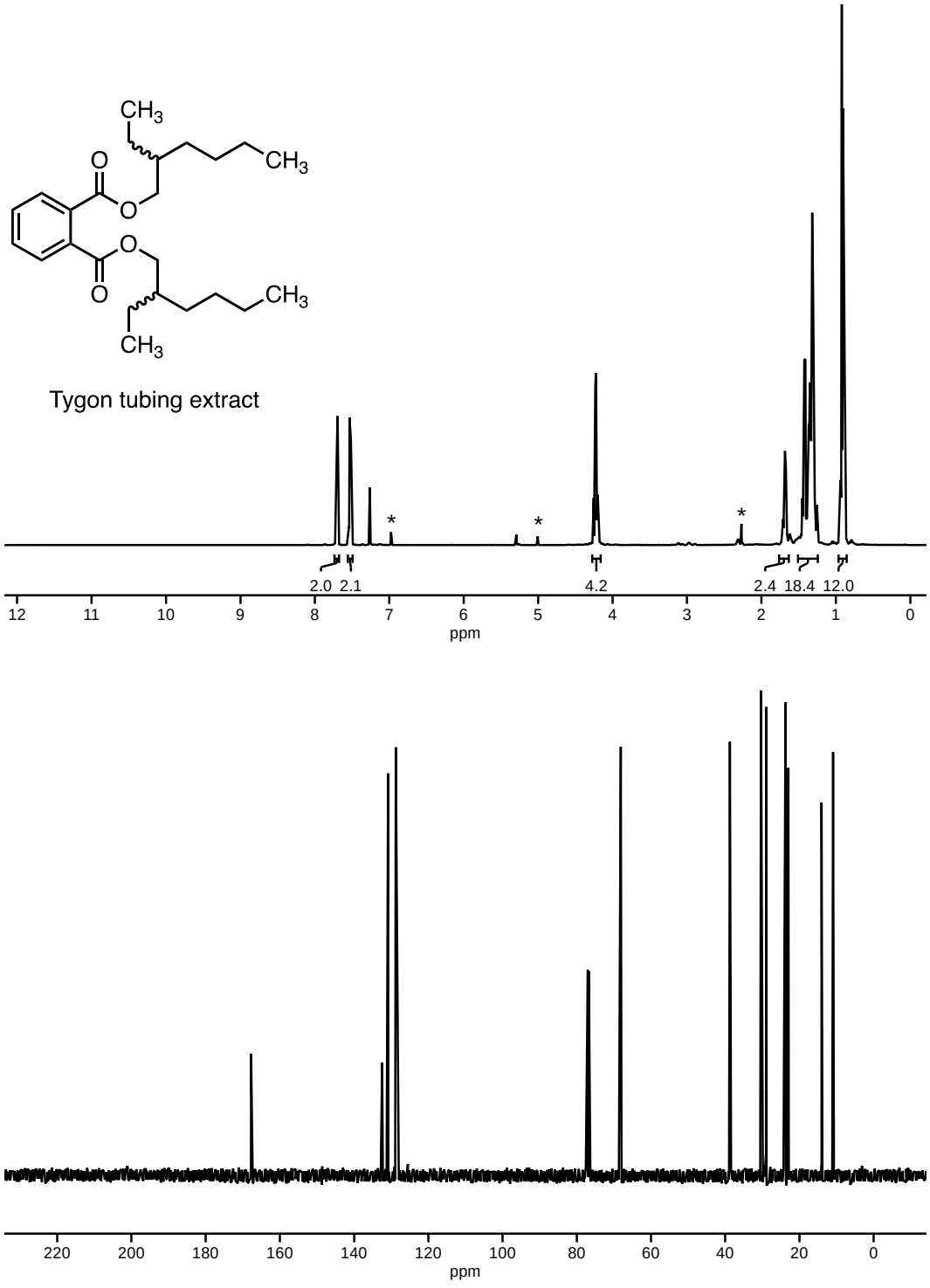


Figure S31. ^{1}H and ^{13}C NMR spectra of Tygon tubing extract. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.68 (m, 2H), 7.56 – 7.49 (m, 2H), 4.27 – 4.16 (m, 4H), 1.76 – 1.63 (m, 2H), 1.51 – 1.24 (m, 16H), 0.96 – 0.85 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.88, 132.60, 131.01, 128.93, 68.28, 38.87, 30.50, 29.06, 23.88, 23.12, 14.18, 11.09. *butylated hydroxytoluene (BHT)

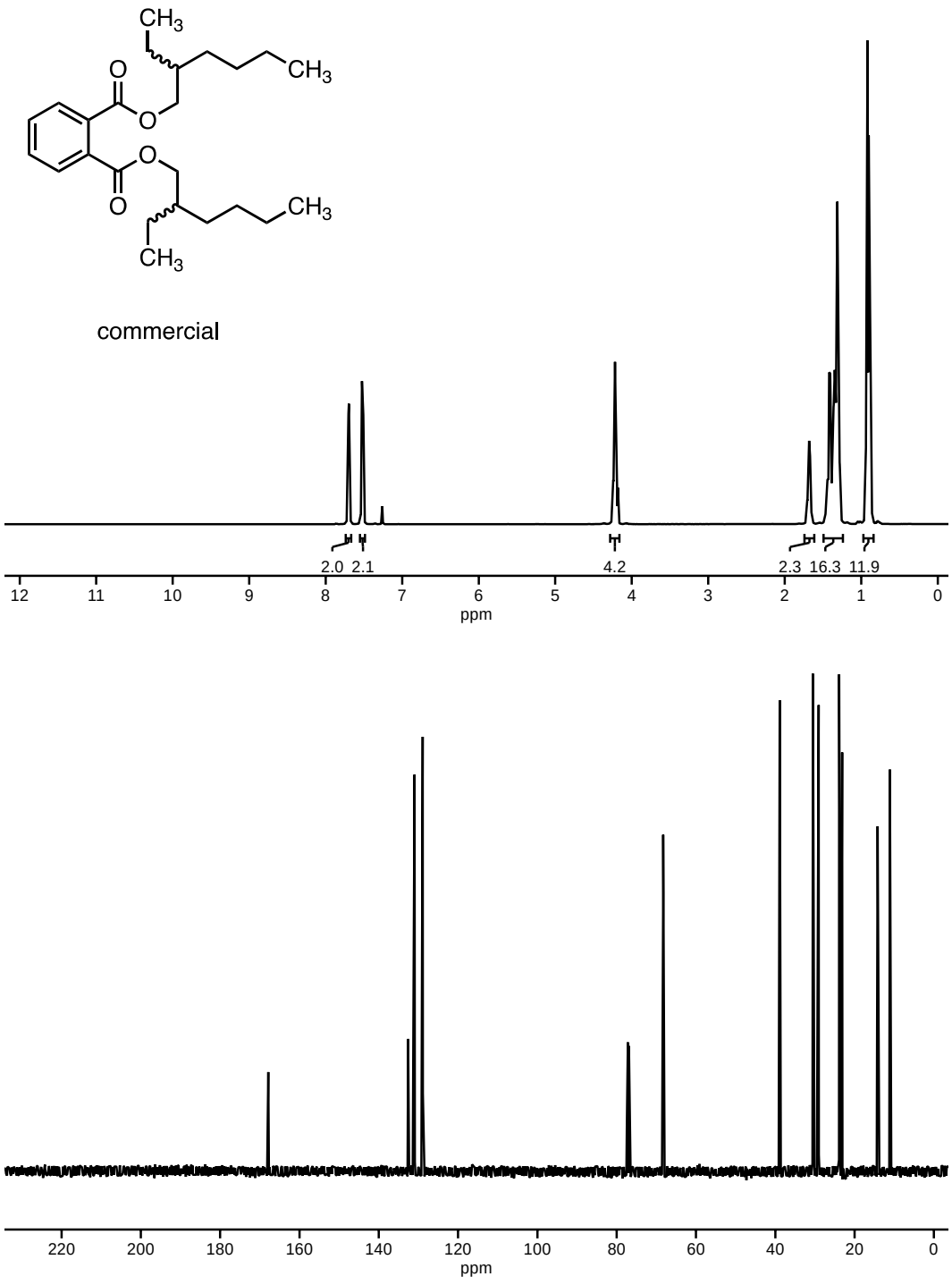


Figure S32. ^{1}H and ^{13}C NMR spectra of commercial **DEHP**. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 – 7.67 (m, 2H), 7.55 – 7.49 (m, 2H), 4.28 – 4.16 (m, 4H), 1.74 – 1.61 (m, 2H), 1.49 – 1.24 (m, 16H), 0.97 – 0.84 (m, 12H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.85, 132.58, 130.98, 128.91, 68.26, 38.86, 30.49, 29.05, 23.88, 23.11, 14.17, 11.08.

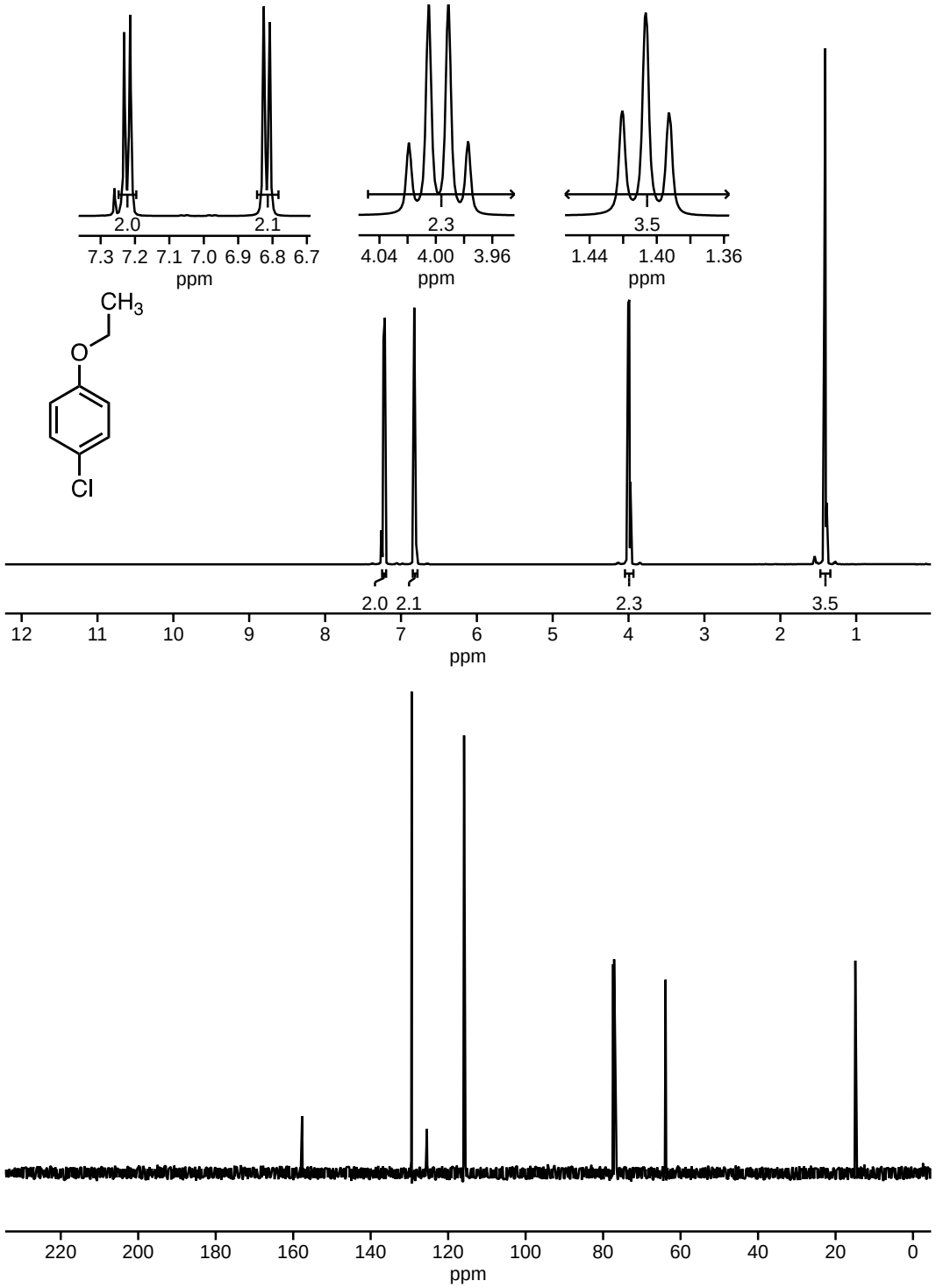


Figure S33. ^{1}H and ^{13}C NMR spectra of 4-chloro-1-ethoxy benzene (**2a**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22 (d, *J* = 8.8 Hz, 2H), 6.82 (d, *J* = 8.8 Hz, 2H), 4.00 (q, *J* = 7.0 Hz, 2H), 1.41 (t, *J* = 7.0 Hz, 3H).^{13}C NMR (126 MHz, $CDCl_3$) δ 157.70, 129.41, 125.49, 115.88, 63.89, 14.89.

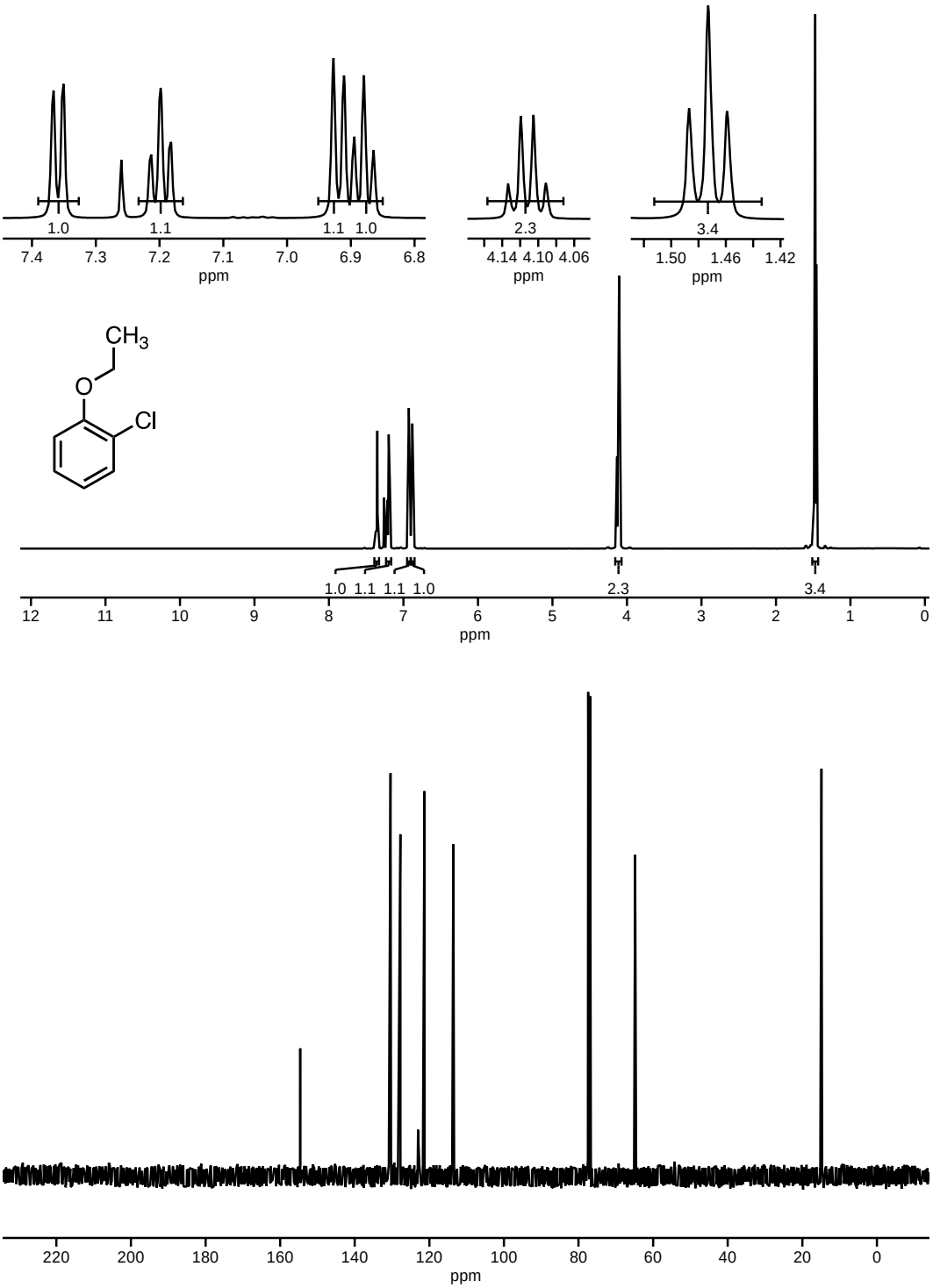


Figure S34. ^{1}H and ^{13}C NMR spectra of 2-chloro-1-ethoxy benzene (**2b**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.8 Hz, 1H), 7.20 (t, *J* = 7.8 Hz, 1H), 6.92 (d, *J* = 8.2 Hz, 1H), 6.88 (t, *J* = 7.7 Hz, 1H), 4.11 (q, *J* = 7.0 Hz, 2H), 1.47 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.62, 130.41, 127.78, 123.01, 121.33, 113.56, 64.81, 14.87.

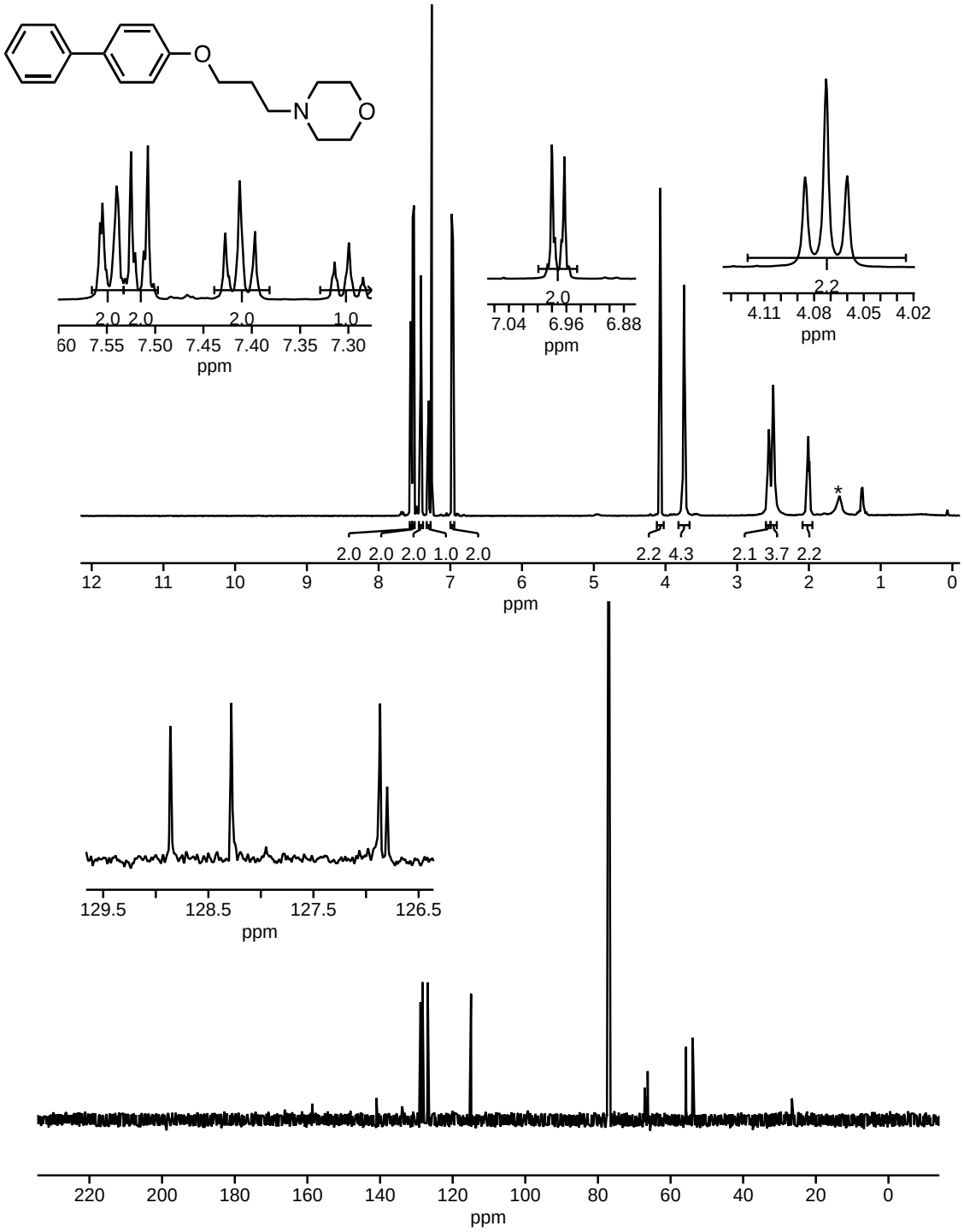


Figure S35. ^{1}H and ^{13}C NMR spectra of 4-(3-([1,1'-biphenyl]-4-yloxy)propyl)morpholine. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 8.2, 1.0 Hz, 2H), 7.53 – 7.50 (m, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.00 – 6.95 (m, 2H), 4.07 (t, *J* = 6.3 Hz, 2H), 3.74 (s, 4H), 2.60 – 2.54 (m, 2H), 2.50 (s, 4H), 2.09 – 1.95 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 158.68, 140.97, 133.91, 128.86, 128.28, 126.87, 126.80, 114.93, 67.10, 66.30, 55.73, 53.89, 26.59. *water

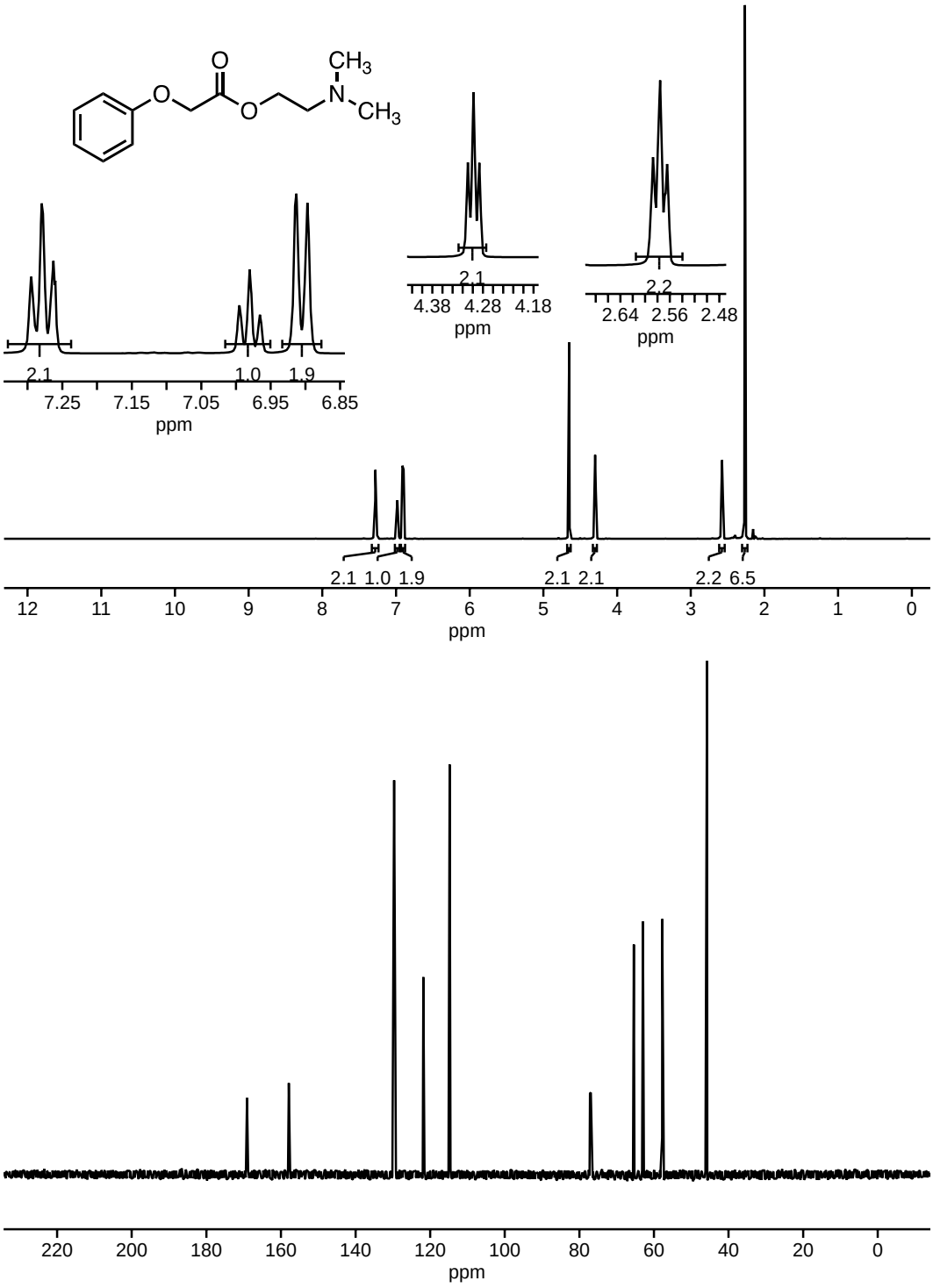


Figure S36. ^{1}H and ^{13}C NMR spectra of 2-(dimethylamino)ethyl 2-phenoxyacetate. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.28 (t, *J* = 8.0 Hz, 2H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 4.65 (s, 2H), 4.30 (t, *J* = 5.7 Hz, 2H), 2.58 (t, *J* = 5.7 Hz, 2H), 2.26 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.11, 157.90, 129.65, 121.82, 114.78, 65.40, 62.95, 57.78, 45.75.

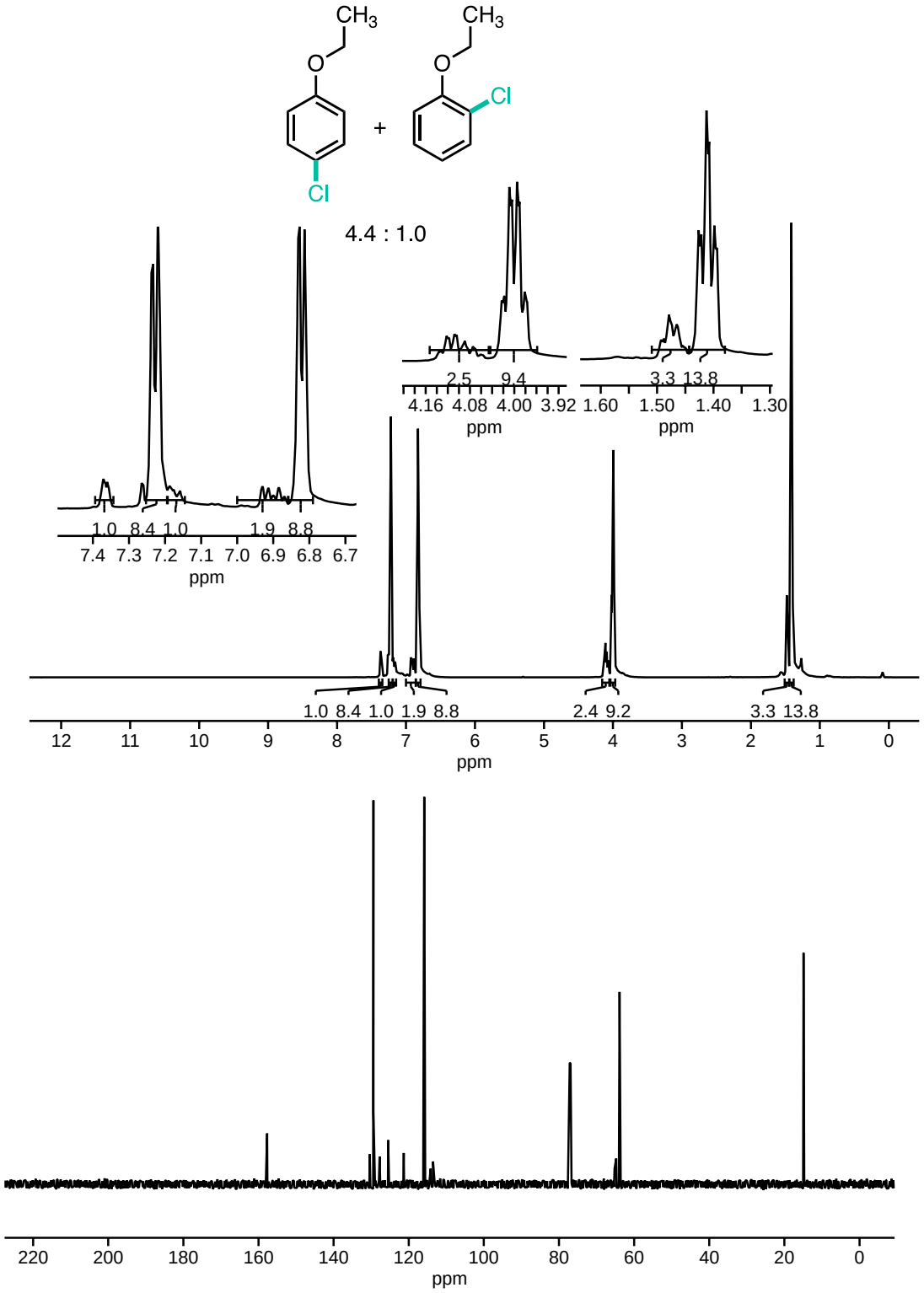


Figure S37. ^{1}H and ^{13}C NMR spectra of 4.4:1 mixture of 4-chloro-1-ethoxy benzene: 2-chloro-1-ethoxy benzene (**2**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (m, 1H), 7.25 – 7.19 (m, 8H), 7.19 – 7.14 (m, 1H), 7.00 – 6.86 (m, 2H), 6.86 – 6.79 (m, 9H), 4.15 – 4.05 (m, 2H), 4.02 – 3.98 (m 9H), 1.47 (7, *J* = 7 3H), 1.41 (t, *J* = 7.0 Hz, 13H). ^{13}C NMR (126 MHz, $CDCl_3$) δ157.69, 130.40, 129.40, 127.77, 125.47, 121.32, 115.87, 113.54, 64.79, 63.88, 14.88.

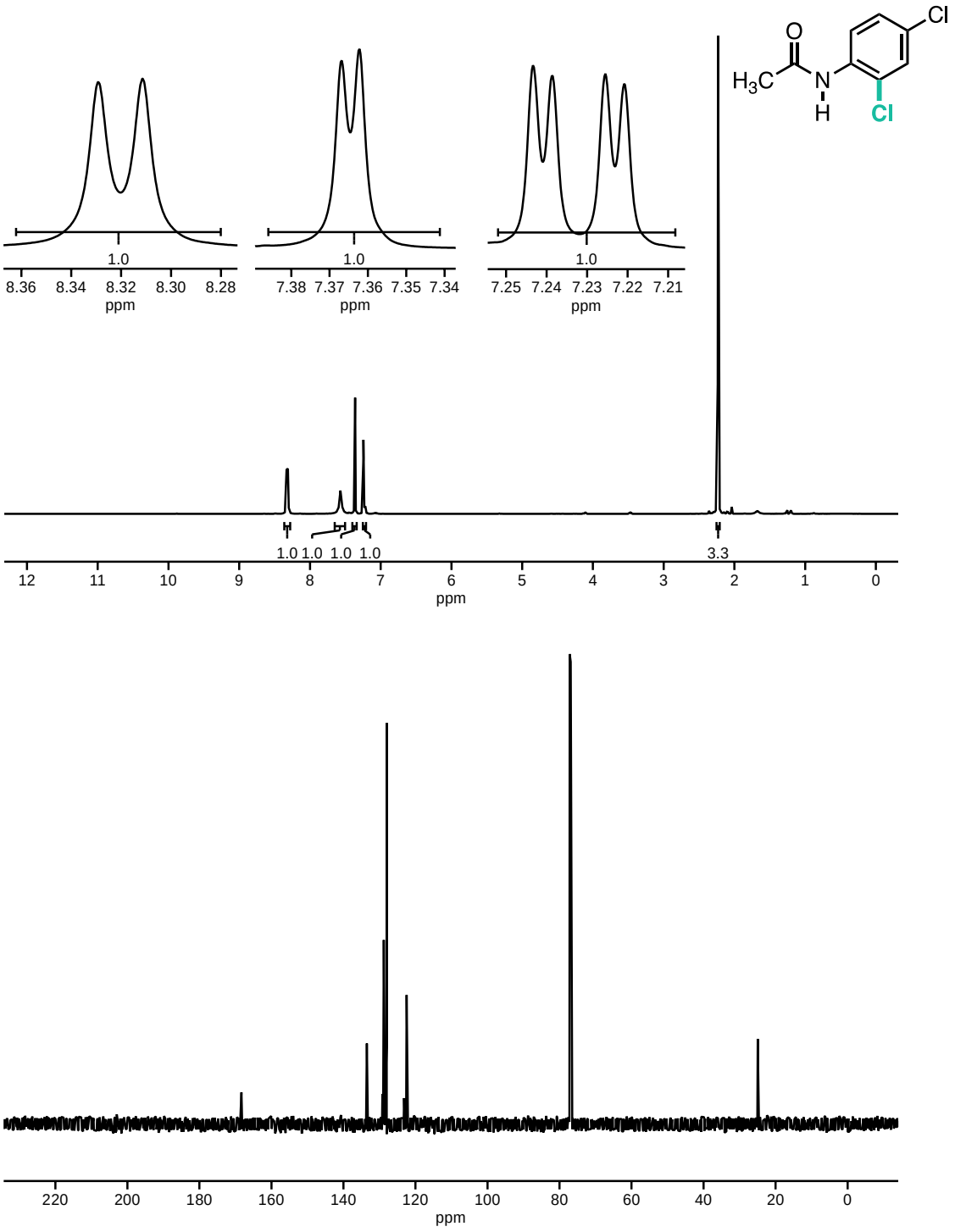


Figure S38. ^{1}H and ^{13}C NMR spectra of *N*-(2,4-dichlorophenyl)acetamide (**3**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.32 (d, *J* = 8.9 Hz, 1H), 7.57 (s, 1H), 7.36 (d, *J* = 2.3 Hz, 1H), 7.23 (dd, *J* = 8.9, 2.4 Hz, 1H), 2.23 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.34, 133.49, 129.17, 128.78, 128.01, 123.16, 122.46, 24.95.

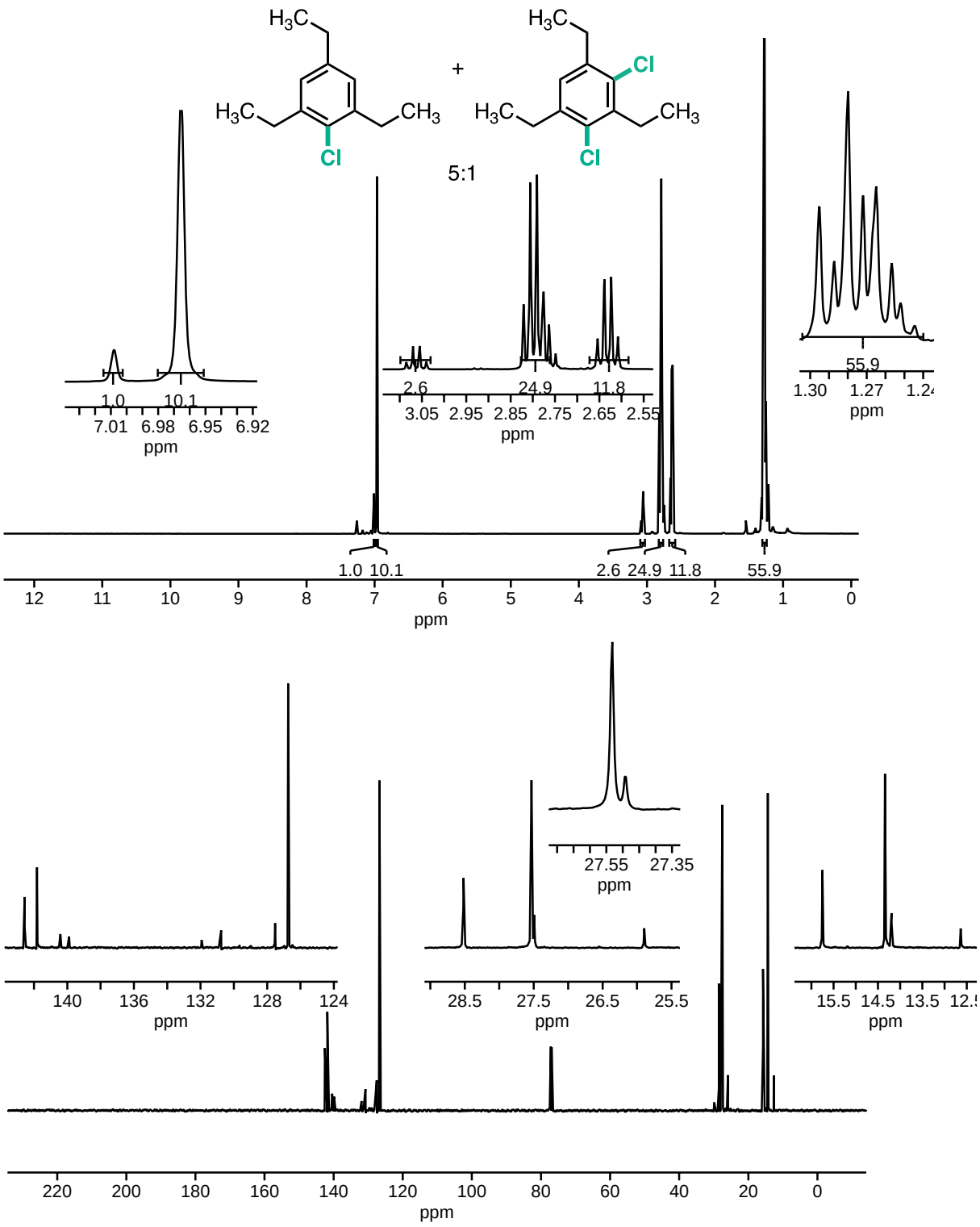


Figure S39. ^{1}H and ^{13}C NMR spectra of 5:1 mixture of 2-chloro-1,3-5-triethylbenzene: 2,4-dichloro-1,3,5-triethylbenzene (**4**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.01 (s, 1H), 6.97 (s, 10H), 3.06 (q, *J* = 7.5 Hz, 2H), 2.80 (q, *J* = 7.5 Hz, 24H), 2.63 (q, *J* = 7.6 Hz, 10H), 1.28 (m, 54 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 142.56, 141.82, 140.41, 139.89, 131.93, 130.76, 127.53, 126.74, 28.52, 27.53, 27.49, 25.89, 15.75, 14.34, 14.20, 12.64.

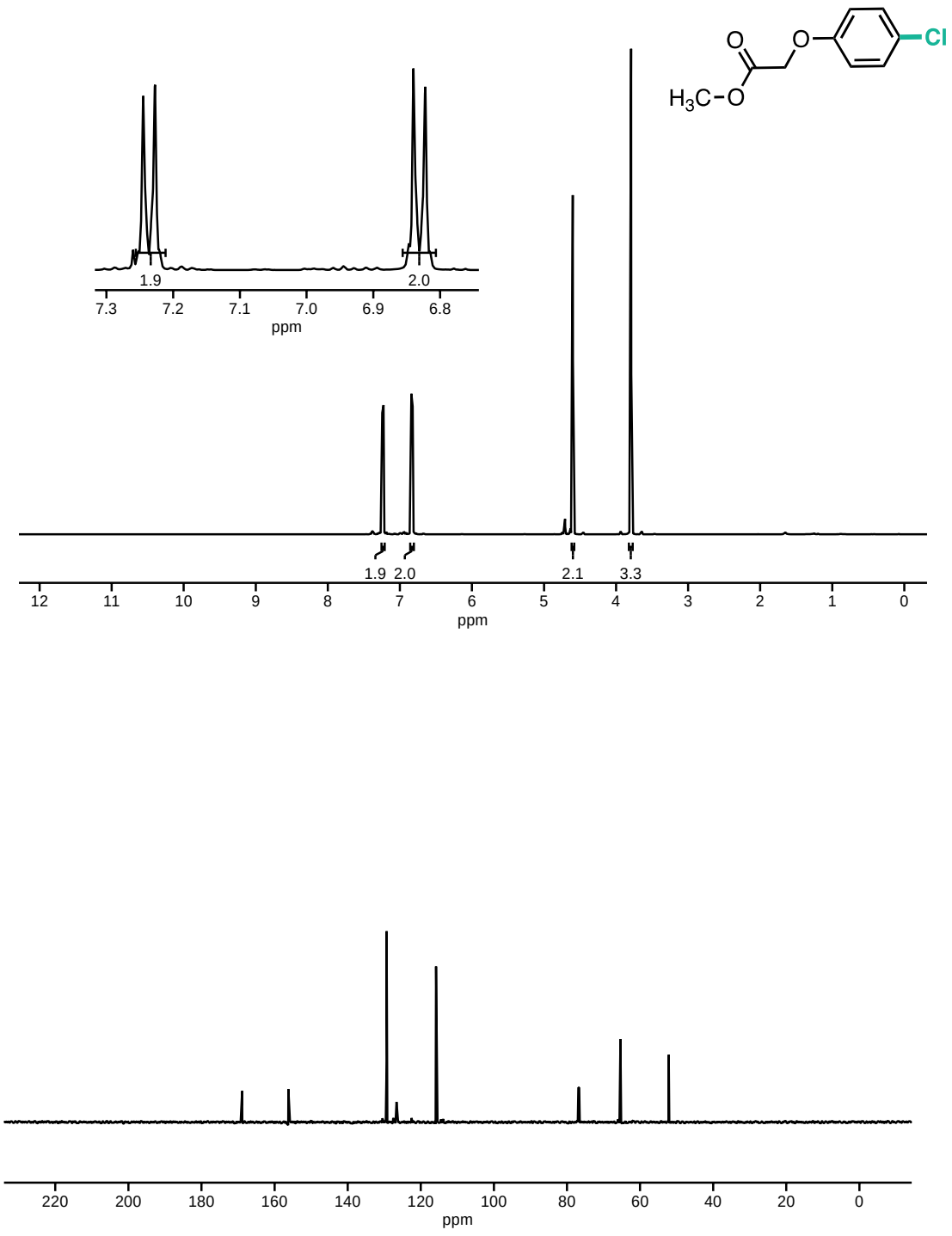


Figure S40. ^{1}H and ^{13}C NMR spectra of methyl 2-(4-chlorophenoxy)acetate (**5**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9.0 Hz, 2H), 6.83 (d, *J* = 8.8 Hz, 2H), 4.60 (s, 2H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.15, 156.50, 129.59, 126.87, 116.10, 65.60, 52.40.

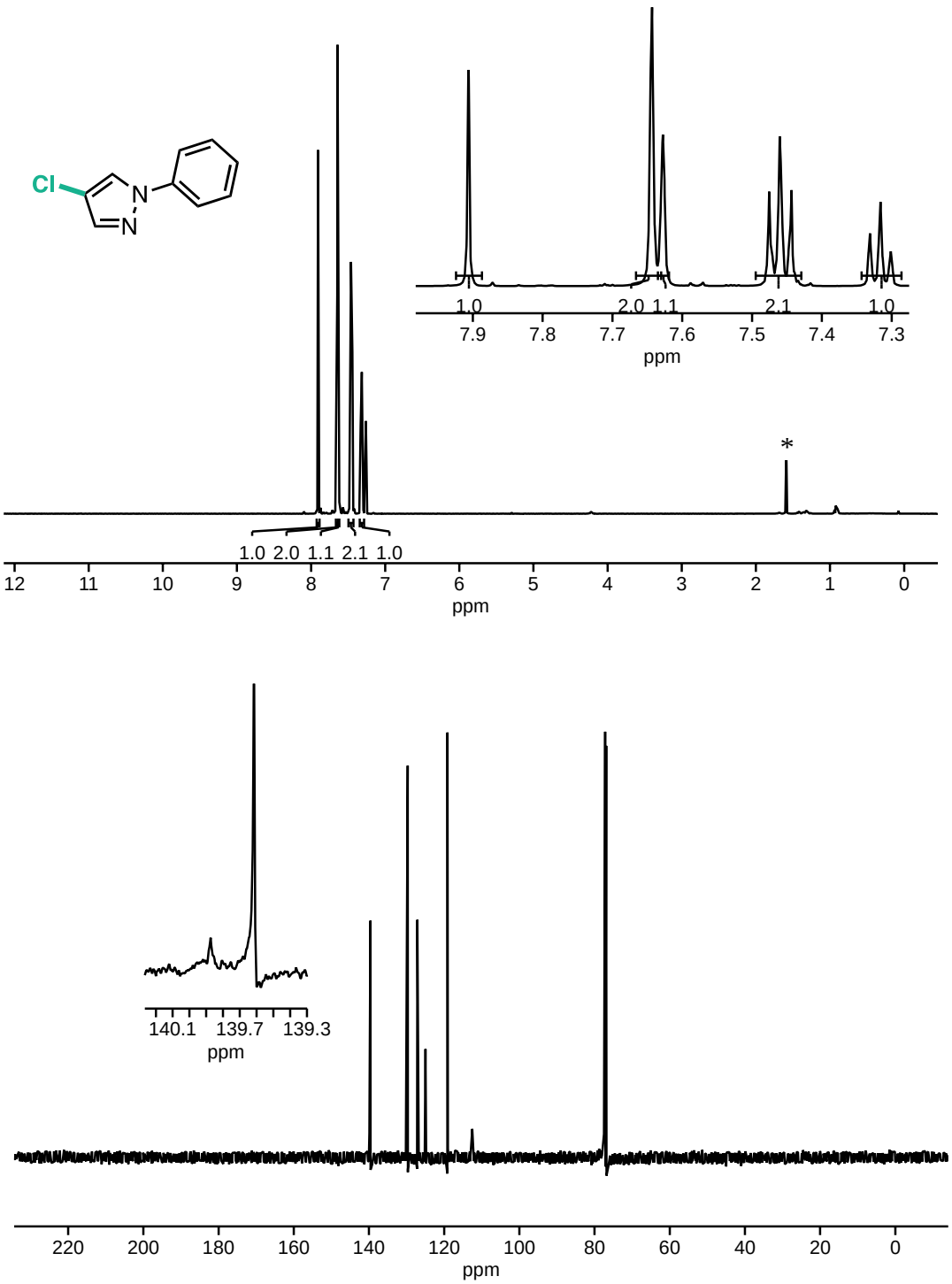


Figure S41. ^{1}H and ^{13}C NMR spectra of 4-chloro-1-phenyl-1H-pyrazole (**6**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.91 (s, 1H), 7.64 (s, 2H), 7.63 (m, 1H), 7.46 (t, *J* = 8.0 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 139.87, 139.62, 129.69, 127.14, 124.96, 119.12, 112.53. *water

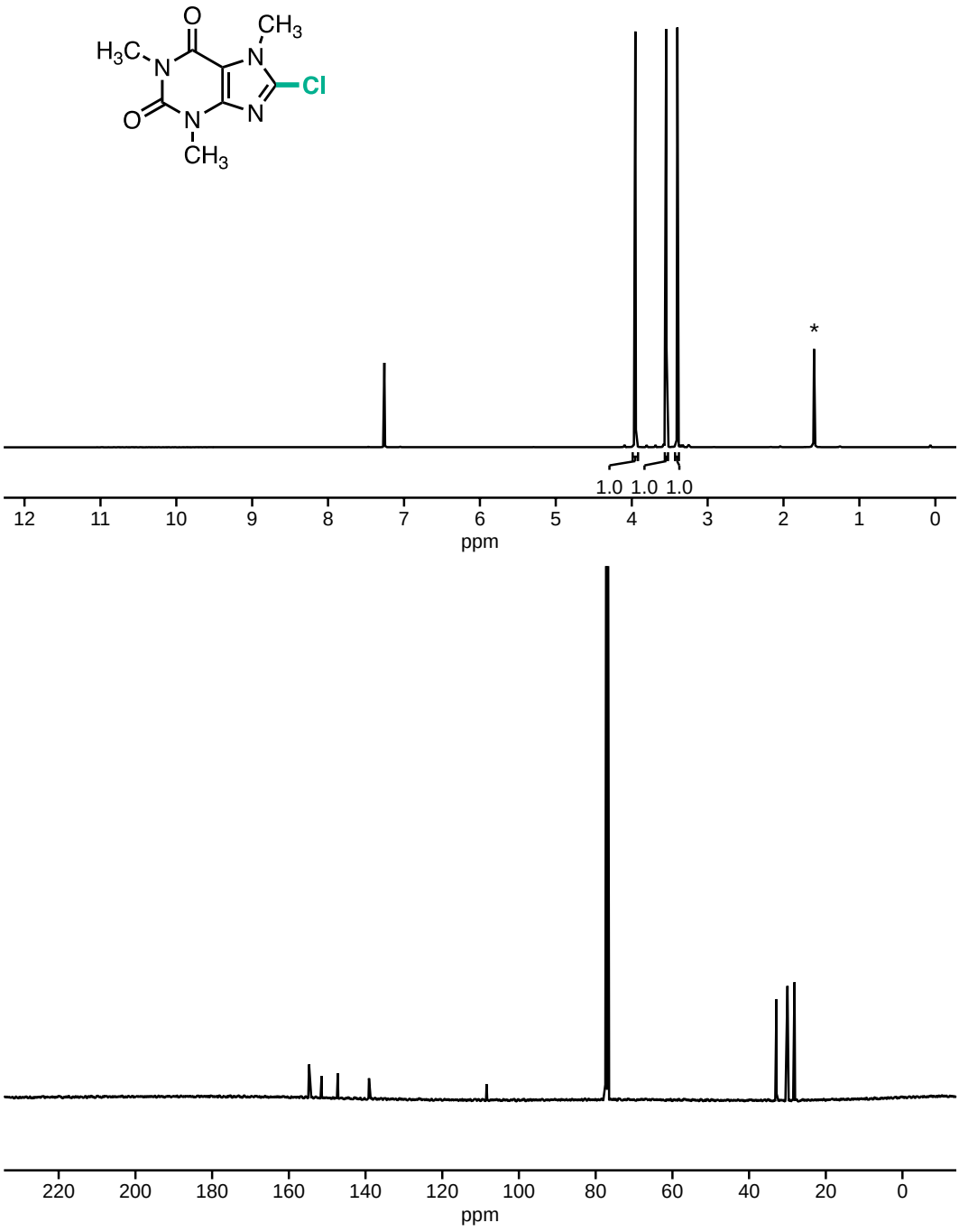


Figure S42. ^{1}H and ^{13}C NMR spectra of 8-chloro-1,3,7-trimethyl-3,7-dihydro-1H-purine-2,6-dione (**7**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.95 (s, 1H), 3.55 (s, 1H), 3.40 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 154.74, 151.45, 147.23, 139.12, 108.41, 32.85, 29.98, 28.16. *water

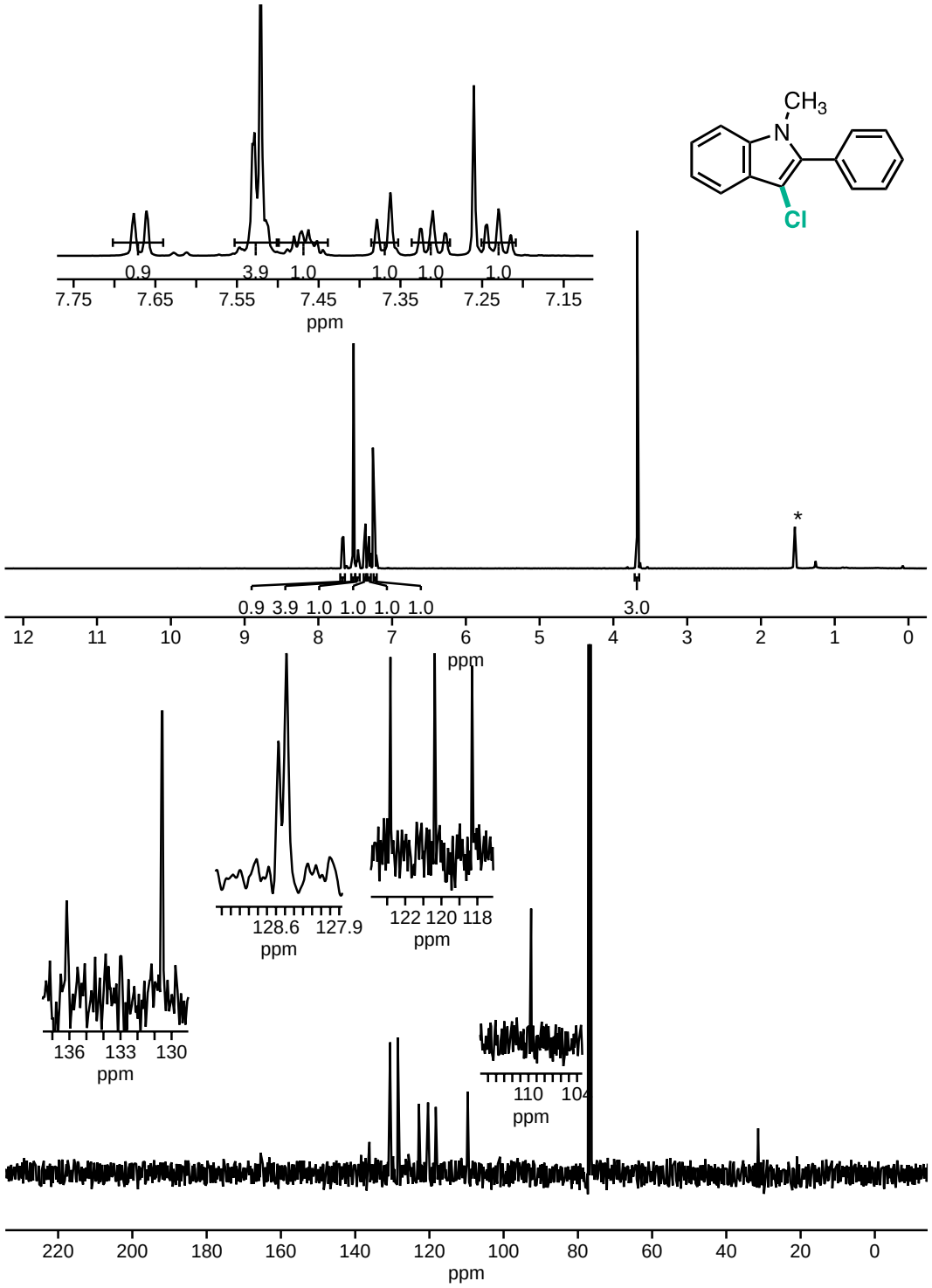


Figure S43. ^{1}H and ^{13}C NMR spectra of 3-chloro-1-methyl-2-phenyl-1*H*-indole (**8**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 7.9 Hz, 1H), 7.52 (m, 4H), 7.46 (m, 1H), 7.37 (d, *J* = 8.2 Hz, 1H), 7.31 (t, *J* = 7.1 Hz, 1H), 7.23 (t, *J* = 7.4 Hz, 1H), 3.68 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 136.17, 130.55, 128.58, 128.48, 125.62, 122.81, 120.36, 118.30, 109.67, 31.46. Note, some expected carbon peaks were not detected at the low concentration. *water

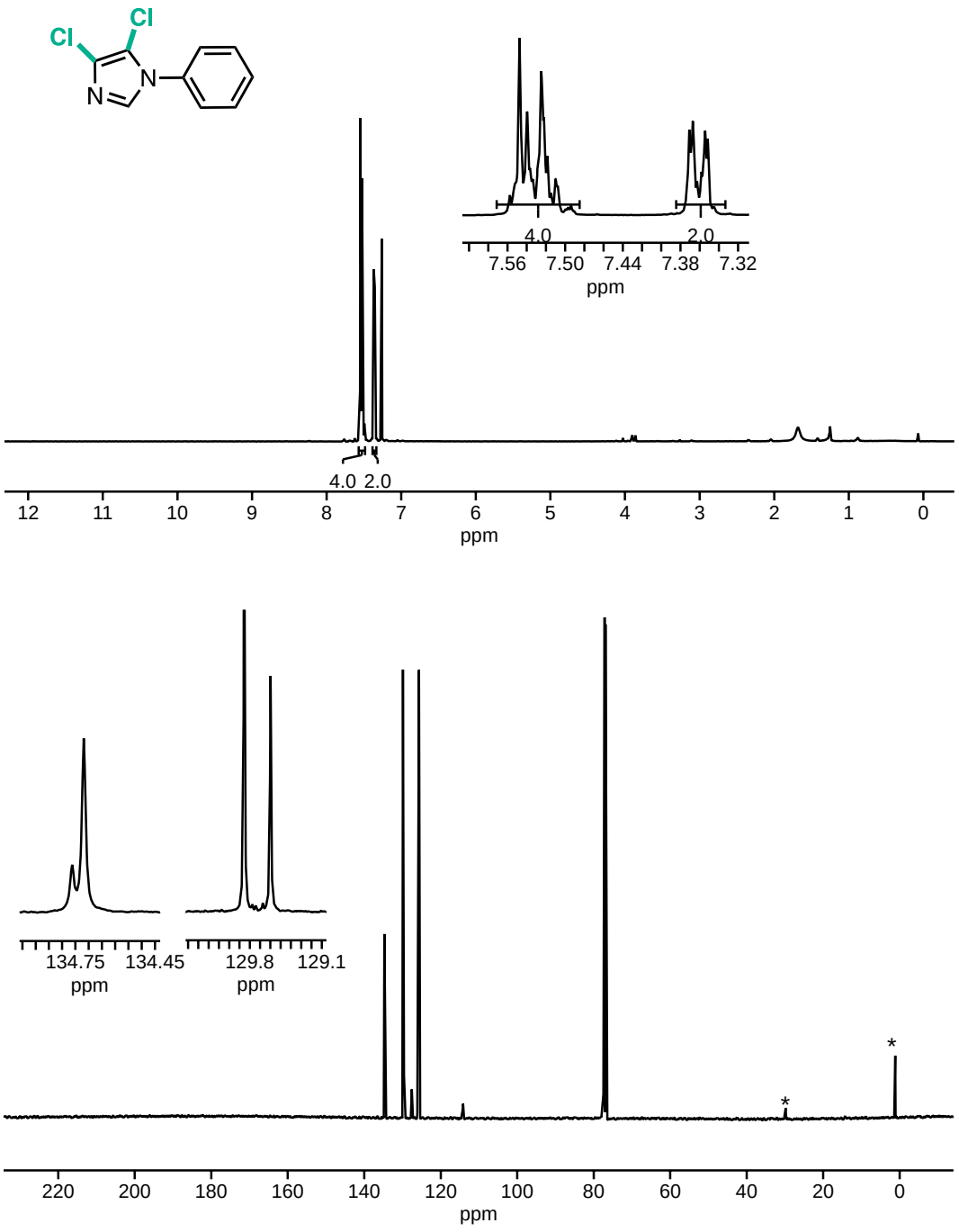


Figure S44. ^{1}H and ^{13}C NMR spectra of 4,5-dichloro-1-phenyl-1*H*-imidazole (**9**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 – 7.48 (m, 4H), 7.38 – 7.33 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 134.76, 134.72, 129.85, 129.60, 127.56, 125.71, 114.16, 29.84. *grease

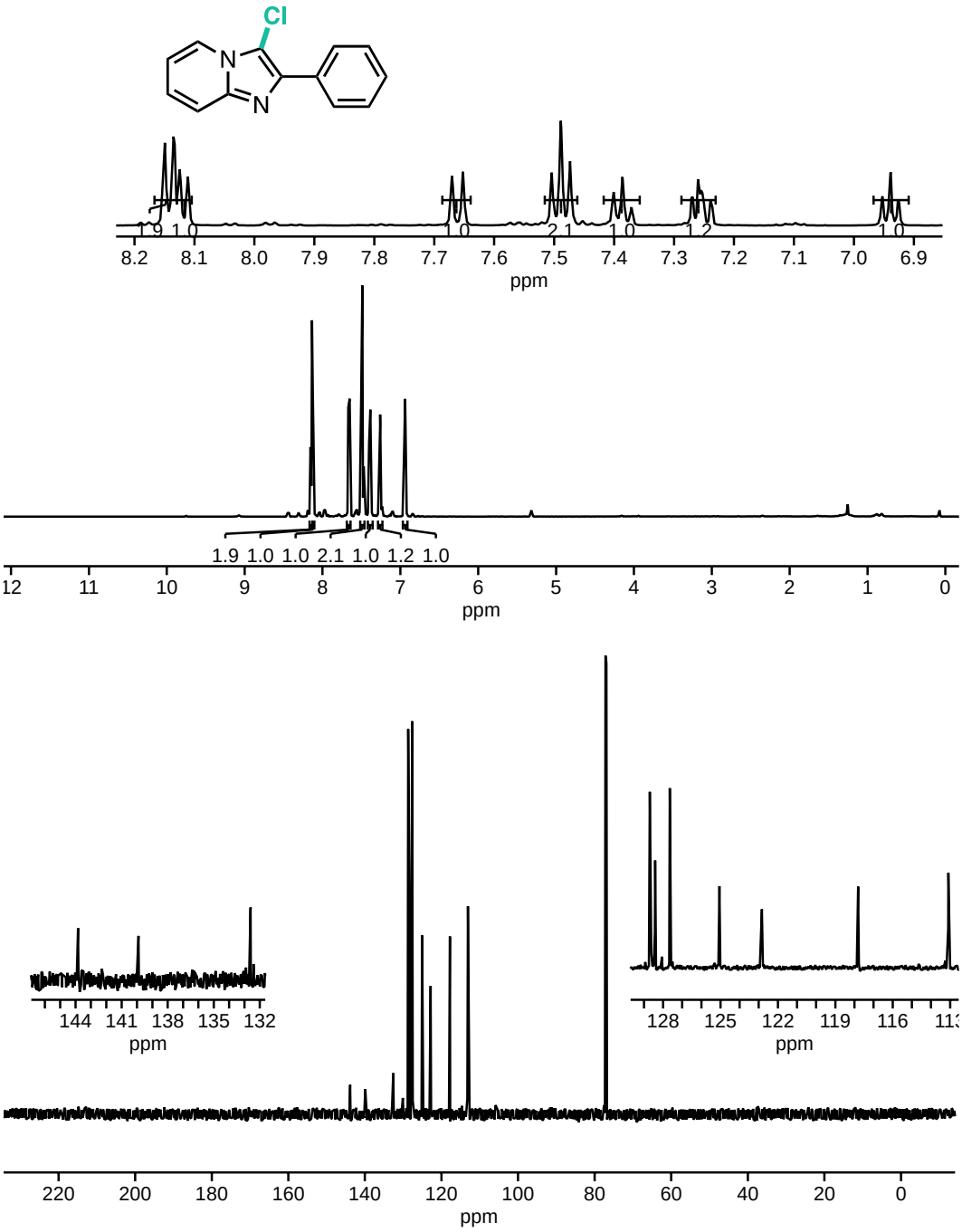


Figure S45. ^{1}H and ^{13}C NMR spectra of 3-chloro-2-phenylimidazo[1,2-*a*]pyridine (**10**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.14 (d, *J* = 7.7 Hz, 2H), 8.12 (d, *J* = 6.9 Hz, 1H), 7.66 (d, *J* = 9.1 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 1H), 7.25 (d, *J* = 16.9 Hz, 1H), 6.94 (t, *J* = 6.8 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 143.84, 139.90, 132.60, 128.70, 128.42, 127.65, 125.05, 122.84, 117.80, 113.10.

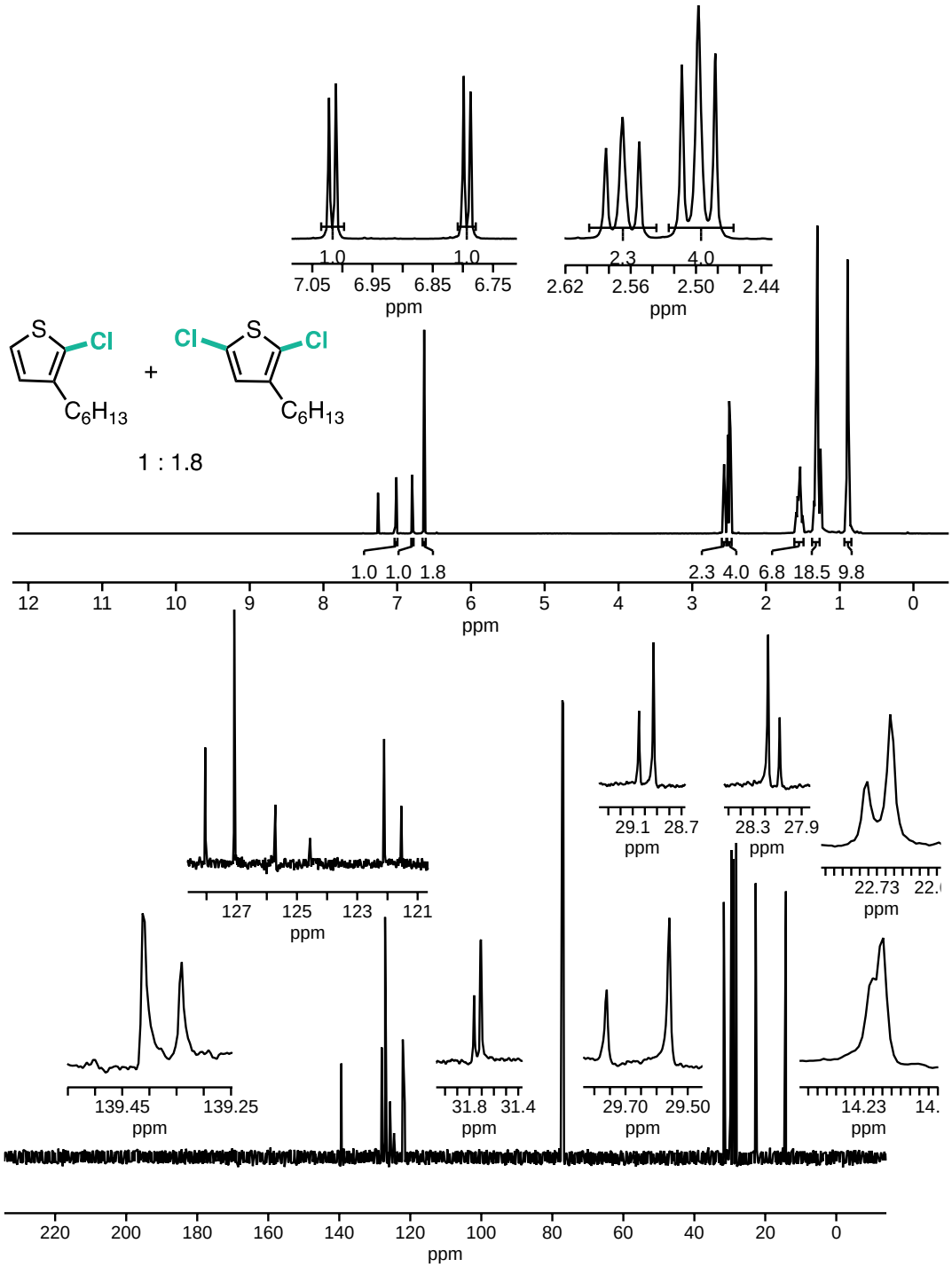


Figure S46. ^{1}H and ^{13}C NMR spectra of 1:1.8 mixture of 2-chloro-3-hexylthiophene: 2,5-dichloro-3-hexylthiophene (**11**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.02 (d, *J* = 5.7 Hz, 1H), 6.79 (d, *J* = 5.7 Hz, 1H), 6.63 (s, 2H), 2.60 – 2.54 (m, 2H), 2.53 – 2.47 (m, 4H), 1.55 (ddt, *J* = 15.0, 12.7, 7.4 Hz, 7H), 1.37 – 1.27 (m, 19H), 0.94 – 0.84 (m, 10H).^{13}C NMR (126 MHz, $CDCl_3$) δ 139.41, 139.34, 128.04, 127.08, 125.72, 124.57, 122.11, 121.54, 31.76, 31.71, 29.76, 29.56, 29.05, 28.93, 28.18, 28.08, 22.74, 22.71, 14.21.

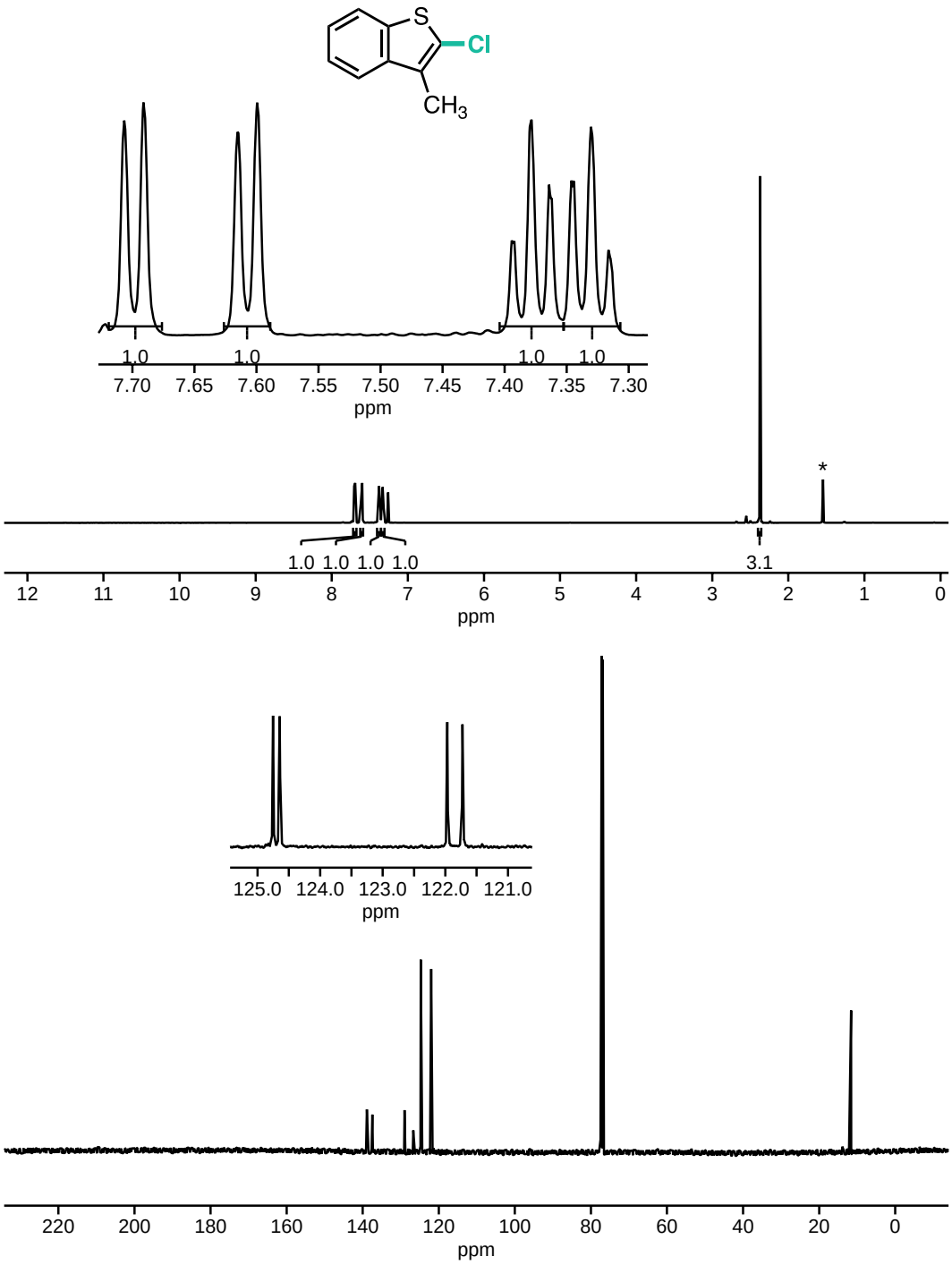


Figure S47. ^{1}H and ^{13}C NMR spectra of 2-chloro-3-methylbenzo[*b*]thiophene (**12**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.8 Hz, 1H), 7.61 (d, *J* = 7.9 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* = 7.0 Hz, 1H), 2.37 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 138.89, 137.46, 129.02, 126.67, 124.75, 124.65, 121.97, 121.73, 11.62.

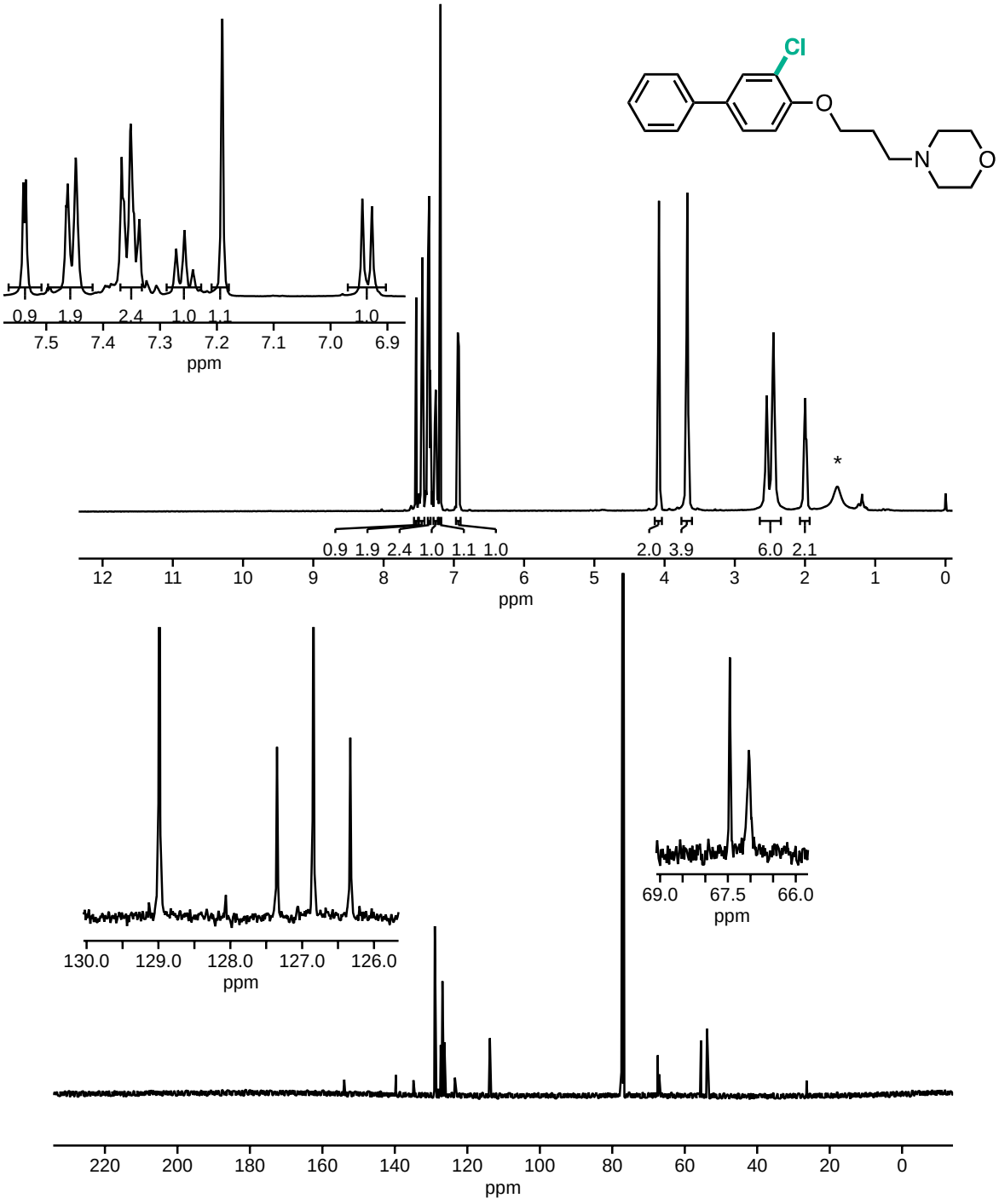


Figure S48. ^{1}H and ^{13}C NMR spectra of 4-(3-((3-chloro-[1,1'-biphenyl]-4-yl)oxy)propyl)morpholine (**13**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (d, *J* = 2.2 Hz, 1H), 7.45 (d, *J* = 7.7 Hz, 2H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 1H), 7.19 (s, 1H), 6.94 (d, *J* = 8.5 Hz, 1H), 4.08 (t, *J* = 6.2 Hz, 2H), 3.68 (s, 4H), 2.50 (m, 6H), 2.07 – 1.93 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.96, 139.72, 134.86, 128.99, 128.06, 127.35, 126.84, 126.33, 123.41, 113.76, 67.46, 67.04, 55.54, 53.85, 26.40. *water

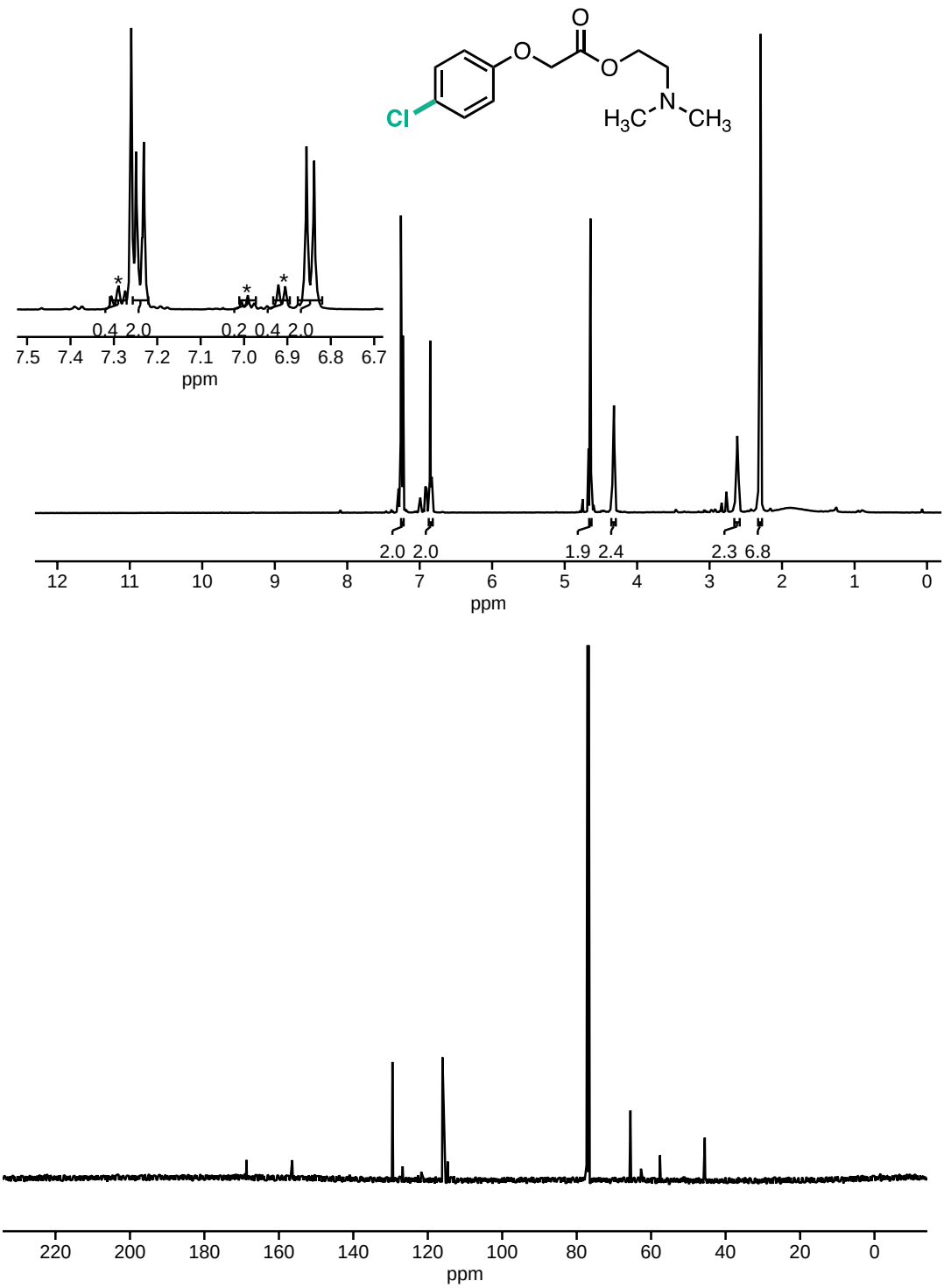


Figure S49. ^{1}H and ^{13}C NMR spectra of 2-(dimethylamino)ethyl 2-(4-chlorophenoxy)acetate (**14**). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 9.0 Hz, 2H), 6.85 (d, *J* = 9.0 Hz, 2H), 4.64 (s, 2H), 4.32 (t, *J* = 5.3 Hz, 2H), 2.66 – 2.58 (m, 2H), 2.30 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 168.68, 156.41, 129.47, 126.74, 116.04, 65.54, 62.74, 57.63, 45.57. *starting material

XIV. References

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